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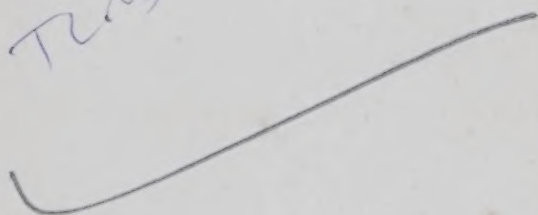
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CHEMICAL AND ELECTRO-PLATED
FINISHES

By the Same Author

THE APPLICATION OF RADIANT HEAT
TO METAL FINISHING (*with J. H. Nelson*)

CHEMICAL & ELECTRO-PLATED FINISHES

The Protective Treatment of Metals

BY

H. SILMAN

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(incorporating the Electrodepositors' Technical Society)

WITH A FOREWORD BY

H. MOORE

C.B.E., D.Sc.

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TO
ALASTAIR McLEOD

FOREWORD

By H. MOORE, C.B.E., D.Sc.

THE regrettable tendency of metals, and especially iron, to return to the oxidised states in which they are found in nature, has given rise to a great variety of processes, old and new, for protecting them from corrosion. A large proportion of these processes consist in coating metals and alloys with more resistant metals by electro-deposition, and a surprising number and variety of protective and decorative electro-plated finishes are now widely used. The coating is usually one metal of high purity, but may be two metals, one superposed on the other, and the electro-deposition of alloys of closely controlled composition is being increasingly employed in industry.

In recent years, the practical improvement of electro-plating processes and the development of new processes has been largely dependent on the scientific study of electro-plating. Research in this subject, as in the wider field of corrosion and its prevention, has made great strides. It is symptomatic of the growing attention given to electro-deposition that the British Non-Ferrous Metals Research Association, which has worked in this field for many years, has lately established a special section for metal finishing research with increased experimental facilities.

A broad review of the subject of protective finishes produced by electro-plating or chemical methods has been a serious need which Mr. H. Silman has now satisfied. In his book, which is both comprehensive and concise, up-to-date and accurate descriptions of processes and equipment are assisted by numerous illustrations and the scientific background and basis are adequately explained throughout. The significance attached to the close connection between theory and practice is indeed a characteristic of the book. The empirical nature of the art of electro-plating in the past has been a barrier between the practical plater and the research man. The work and publications of the Electrodepositors' Technical Society and the American Electroplaters' Society are two agencies tending to break down this barrier, and Mr. Silman's book gives powerful help. Electro-plating is losing the mystery and secrecy which used to surround it and has become a scientifically understood and controlled branch of technology.

The author never loses sight of the practical needs of designers,

manufacturers and users concerned with electro-plating and allied processes. The book should make a special appeal to two classes of technical men, the practical plater who not only requires guidance on processes, possibly new to him, but also wishes to acquire some basic understanding of what he is doing, and the works chemist, metallurgist, or engineer, who has not specially studied electro-deposition but is charged with some supervisory responsibility for electro-plating and metal finishing among other production processes. These two classes are indeed drawing closer, and are more able to understand each other's language and point of view, as scientific and technological education spreads among the practical electro-platers. The chemist in charge of process control is also learning to value more highly the skill and accumulated experience of the plater.

The study of phenomena and reactions occurring at interfaces between solids, liquids and gases has grown into one of the most significant and many-sided branches of physical chemistry. Corrosion, the attack of metal surfaces by their environment, is a surface problem of the utmost practical importance, and its general consideration in the first chapter is a useful review of the main facts in the light of the scientific principles now established. The production of chemically clean metal surfaces, polishing, and the formation of protective coatings are similarly treated in succeeding chapters. Naturally, in a book of moderate size and so wide a scope as Mr. Silman's, it is not possible to give an advanced treatment of the many problems in surface physical chemistry arising. Serious students of the science of surfaces will, however, gain from the book an excellent perspective of the wide practical field of surface chemistry with which it deals, and will especially appreciate the numerous references.

The combating of corrosion of metals and alloys by the application of protective coatings is now a matter of prime concern in almost every branch of engineering, while its domestic and architectural importance is even more evident to the general public. Many classes of readers will find much of value, interest, and profit in Mr. Silman's book, with its wealth of practical detail combined with a thoroughly scientific treatment.

H. M.

September 1947

PREFACE TO THE SECOND EDITION

In the short time which has elapsed since the appearance of the first edition of this book rapid developments have occurred in metal protection and plating which have necessitated substantial additions to the text, and a thorough revision of the contents. In particular, the diagrams and illustrations have been revised with the object of visually setting down before the reader examples of the best modern practice in the metal finishing field. The increasing interest in metal finishing is shown by the number of new journals now being published with the aim of disseminating information on this subject. This is all to the good, and serves to emphasise that this is a field in which great improvements in quality and reduction in costs can be achieved by the use of good methods.

The need for bringing British industries to the highest pitch of efficiency means that we can afford to employ only such methods and equipment as are completely modern and not wasteful of time, labour or materials; all others are too expensive.

In this edition the original objectives of the book have been kept unchanged, and the author hopes that the reader will find a highly concise, yet clear and adequately detailed, account of the best current ideas and practice in this important branch of industry. The chief difficulty in preparing this edition has been to ensure that the material is complete and up to date because of the speed with which new developments are being introduced, and in this the author hopes he has succeeded.

•
H. S.

BIRMINGHAM

February 1950

AUTHOR'S PREFACE

It is only in the comparatively recent past that electro-plated and allied finishes have become the subject of serious scientific investigation, but already the results obtained are indicative of the immense value which can accrue to industry as our knowledge of the processes involved increases. This book is intended to cover a well-defined field, viz. the finishes which are commercially applied to metals for decorative and protective purposes from aqueous solutions with or without the use of electric current. These finishes can be conveniently grouped together as they constitute an integral and essential part of present-day engineering technique. It is by no means uncommon to come across instances where failures occur in units of otherwise admirable design and construction due to inadequate protection against corrosion and abrasion. Whilst in some instances this is due to failure to make use of the best current practice, in others a solution to the problems involved has yet to be found. Not the least of the difficulties in the manufacture of jet propulsion units and in the development of atomic power for example, is the question of protection for the metals employed.

The literature on the subject of chemical and electro-plated finishes is widely scattered, except for a few journals which are too highly specialised to be generally read by engineers. In this volume an attempt has been made to present a reasonably comprehensive account of modern industrial finishing processes, together with the chemical and physical principles involved in them. In this respect the book is intended to cover the gap between text-books of applied electro-chemistry and available publications on the practice of electro-plating. With a few admirable exceptions the former do not do justice to industrial electro-deposition whilst the latter often lag behind the best modern practice and do not adequately cover the non-electrical treatments or the chemistry involved in a proper understanding of them.

To accomplish this object in a volume of reasonable dimensions and to give the busy technical reader a correct perspective of the subject has been no easy task. It has involved the elimination of all discursive writing and only passing reference to obsolete or obsolescent processes. Likewise, processes which are not in current use in industry and are not likely to become established in the not-too-distant future have also been restricted in the space allotted to them.

In this way it is hoped that the reader will find an adequately detailed though concise account of those aspects of the subject in which he is interested.

It has also not been a simple matter to determine the extent to which chemical and electro-chemical theory should be introduced; it was decided to avoid entering into a detailed fundamental study of the subject such as could be obtained from a text-book but to include sufficient for an appreciation of the principles on which the processes described are based. No proprietary product is referred to without some indication of its composition; in the case of proprietary processes these again are only mentioned when an account of the chemical principles on which they are based can be given.

The requirements of engineers and designers and of those concerned more directly with the scientific and technical aspects of metal finishing both from the process and plant angles have been borne in mind. The chemical and mechanical engineering problems involved in plant construction are of increasing importance as the industry tends to change from the simple manual handling of articles into and out of solutions by skilled workers to fully mechanised automatic units carrying out a pre-determined cycle of operations. These changes are resulting in a demand for more chemists and engineers to help solve the multifarious problems involved, although the number of first-class scientists who have been attracted to this fascinating field of work is still regrettably small.

In many respects American practice is ahead of ours in the finishing field and it was therefore especially fortunate that the opportunity arose for making an extended visit to the United States whilst the book was passing through the press. It was thus possible to increase its value by incorporating particulars of some of the newest American developments and to ascertain by first-hand contact that the sections dealing with American practice accurately reflect the technical picture in the United States.

On points of detail, it has been decided to employ both the C.G.S. and Imperial systems of measurement to avoid conversion of quoted data into awkward fractional quantities. The term "gallon" refers to the Imperial gallon throughout the book, however.

The subject of analysis of plating solutions has not been included as it is of specialised interest and is, moreover, adequately covered in existing publications.

ACKNOWLEDGMENTS

Thanks are due to my many friends in the industry whose advice and experience have helped so much in the writing of this book. To Messrs. W. Canning & Co. Ltd., I am grateful for illustrative material and for enabling me to draw on their prolonged experience of the practical aspects of electro-plating. Mr. Alan Smart, of the Electrochemical Engineering Co. Ltd., has given willing advice on the mechanical engineering problems involved in the construction of automatic plating plants, whilst Messrs. Nordac Ltd. have helped on problems pertaining to the use of rubber-lined plant in pickling and plating practice. The chapter on nickel-plating owes much to Dr. S. Wernick with whom it was my privilege to collaborate on some of the early work in this country on the bright nickel-plating of zinc-base die-castings and on overcoming the difficulties of solution filtration and purification as applied to nickel deposition.

The publications of the Electrodepositors' Technical Society, the Electrochemical Society and the American Electroplaters' Society have also been drawn on extensively.

I also gratefully acknowledge the facilities put at my disposal by numerous American authorities to help in filling the large gaps in my knowledge of American finishing practice. In particular, the generous assistance given by Dr. Louis Weisberg, Dr. M. B. Diggin, of the Hanson-van Winkle-Munning Co., Dr. C. L. Faust and Dr. Bruce Gonser of the Battelle Memorial Institute, Mr. M. W. Phillips, of the General Motors Corporation's Central Research Laboratories and Dr. A. K. Graham, Executive Secretary of the American Electroplaters' Society, must be placed on record. Many other commercial organisations including the Udyllite Corporation, the Parker Rustproof Company and the Detrex Corporation, have also contributed to the completeness of this survey.

To my colleagues both past and present, and particularly to the staffs of the research, process planning and manufacturing departments of Messrs. Joseph Lucas Ltd. and associated companies, I owe a great deal for their willing co-operation in both laboratory and plant experimental work. Much of this was made possible by the provision of the necessary facilities for research and development on finishing processes by the directors of the company.

To Messrs. Industrial Newspapers Limited and to Mr. Alastair

McLeod, their Managing Editor (Technical), thanks are due for the loan of blocks and for permission to reproduce material which was originally published in *Sheet Metal Industries*. Dr. H. Moore has my gratitude not only for his kindness in writing the foreword, but also for some helpful suggestions.

To Miss Dorothy Wernick, B.Sc., A.R.I.C., I am indebted for help with the book during the proof stages and in the preparation of the indexes.

H. S.

September 1947

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THE CORROSION OF METALS AND ALLOYS

One of the features of technical development during the past few decades in the engineering field has been the rapid growth in the use of metals and alloys, and the advent of new methods for the manufacture and fabrication of metal parts; thus zinc entered into a largely new field when it appeared as the main constituent of zinc-base die-castings, while iron is now in the early stages of its use in the production of pressed and sintered metal parts. With these advances came great progress in assembly processes, such as spot-welding, copper-brazing, and a host of others. All these developments presented their own finishing problems, many of them difficult ones, which had to be overcome. Some of the recently developed alloys are highly durable and corrosion-resisting; others, again, are susceptible to weather and corrosive conditions generally, from which protection is required. Notable amongst these are many of the light alloys, and the development of successful methods for protecting these represents a major technological achievement.

Apart from this, strides have also been made independently in the methods of finishing the older and most commonly used metals, such as iron and steel. Thus the synthetic resins have enabled far better and more rapidly applied paints and varnishes to be produced, while in the field of electro-plating new plant developments and electro-chemical research have increased the range of usefulness of electro-deposits beyond recognition.

The art of metal finishing concerns itself with processes involving the application of treatments or materials to the surfaces of metal parts to increase their durability or to improve their appearance. Most metals in common use are liable to attack by the atmosphere or other agencies which may cause serious damage to parts made from them unless precautions are taken to reduce the tendency for such corrosion to occur. Even when deterioration of the metal surface is not dangerous and will not impair the working of the unit, the effect is generally unsightly. In selected cases, on the other hand, corrosion products are considered attractive (e.g. the green patina on old copper) and may exercise some protective value also. (See p. 14.)

Finishes are applied to metal for three main purposes, some or all of which may be operative in particular cases:

- (1) For protection against corrosion.
- (2) For decorative purposes.
- (3) For increasing the wearing qualities of the metal surface.

The first is, perhaps, the most important, especially in the case of iron or steel articles.

It is often possible to improve the appearance of metal articles greatly by the careful selection of a finishing treatment. An improvement in wear-resistance is sometimes directly sought, as in the hard chromium-plating of tools; in other cases it is incidental, as, for instance, when soft zinc-base die-castings are chromium-plated, not only is their appearance improved, but they are also protected against corrosion and given a much harder wearing surface than the original metal possesses.

Some Fundamental Principles of Corrosion Phenomena.—

Without some understanding of the characteristics of corrosion phenomena, it is difficult, if not impossible, to appreciate the principles upon which sound metal finishing treatments are based. By corrosion is meant the destruction of a metal as a result of the action of chemical or electro-chemical agencies. Atmospheric corrosion is a result of a combination of the effects of the following factors:

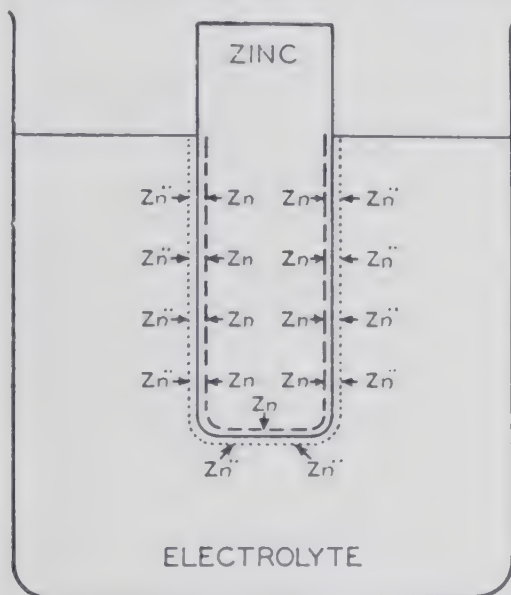
- (a) The oxidising action of the air itself.
- (b) The effect of water vapour and possibly of condensed moisture.
- (c) The presence of corrosion-accelerating substances in the air, e.g. salt in marine atmospheres, and dusts or sulphur containing gases in industrial atmospheres.

Corrosion may also occur due to conditions other than exposure to the atmosphere, e.g. in the case of steel exposed to the action of solutions which will attack the metal directly. Although metals in use in industry are subjected to a variety of special corrosive conditions, e.g. attack by acids, oxidation due to high temperatures, etc., the main concern of the metal-finishing industries is with protection against deterioration due to atmospheric corrosion in all its aspects. Atmospheric corrosion itself is a wide field, and the present survey will, therefore, mainly confine itself to this type of corrosion, and will only deal incidentally with the action of specific chemical agencies.

Electro-chemical corrosion is sometimes said to occur chiefly under conditions of total immersion where electrical currents can be set up in solutions, while direct chemical corrosion is largely confined to conditions of exposure to gases and corrosive vapours. This

distinction is, however, not by any means a hard-and-fast one, and a variety of complicating factors prevent any such clear-cut distinction being drawn.

Generally speaking, metals are not subject to corrosion unless there is a certain amount of moisture present. Vernon⁽¹⁾ has found that there is a critical humidity at which corrosion becomes rapid;



SINGLE ELECTRODE POTENTIAL

$Zn \rightarrow$ SOLUTION PRESSURE OF ZINC

$Zn'' \rightarrow$ OSMOTIC PRESSURE OF ZINC IONS

----- NEGATIVELY CHARGED LAYER

..... POSITIVELY CHARGED LAYER

Fig. 1.—Single electrode potential of zinc

below this any corrosion which does occur in the presence of oxygen is extremely slow. The critical humidity value is that at which the corrosion-product becomes capable of absorbing moisture. On the other hand, in the presence of hygroscopic salts (e.g. magnesium chloride) in the pores of a metallic surface, atmospheric corrosion may set in at humidities considerably below the "critical" value. Thus a piece of cast iron or steel which has been immersed in the sea for a long period and is then brought out, dried, and left in an ordinary room will be found after a few days to be covered with globules of water each of which is coated with a spherical membrane

of rust. This penetration of pores in the metal by hygroscopic salts is often sufficiently powerful to cause the material to break up into laminae or even to disintegrate altogether.

There are a number of factors which will influence corrosion of a metal. The first, which has received a great deal of attention and upon which much fundamental research work has been carried out, is the electro-chemical potential or electrode potential of the metal concerned.

Nernst pointed out that every metal has a definite tendency to pass into solution in the form of ions when immersed in an aqueous solution of one of its salts. Simultaneously the osmotic pressure of the ions in the solution results in a corresponding tendency for the ions to pass out of the solution on to the metal surface. If the solution pressure of metal is greater than the osmotic pressure of the ions the metal will tend to pass into solution. Thus, when zinc is immersed in an aqueous solution of one of its salts, positively charged zinc ions enter the latter, with the result that the metal acquires a negative charge (see Fig. 1). On the other hand, a less electro-negative metal, such as copper, under similar conditions causes the discharge of the positive ions on to the metal surface, so that the copper electrode acquires a positive charge. Simultaneously, a depletion of ions occurs in the solution in the neighbourhood so that a negatively charged solution film exists in close contact with the copper surface due to a local preponderance of anions.

These single-electrode potentials, as they are often termed, are capable of direct measurement and are conventionally determined against the normal hydrogen electrode taken as zero.

The Electro-chemical Series.—A table can then be constructed of the normal electrode potentials of a whole range of metals. Some single-electrode potentials are given in Table I; the determinations are made with the metals in contact with normal solutions of their ions. A change in the ion concentration will show itself by a variation in the electrode potential.

This arrangement of electrode potentials is termed the Electro-chemical Series. In more complete tables⁽²⁾ it will be found that figures are quoted for extremely electro-negative metals such as sodium and potassium. These cannot be determined experimentally owing to their reactivity with aqueous solutions. They may, however, be calculated from theoretical considerations.

Certain other metals give results which do not represent the true electrode potential when experimental determinations are carried out.

TABLE I
SINGLE-ELECTRODE POTENTIALS

Metal	Volts
Gold . . .	+ 1·36
Platinum . . .	+ 0·860
Silver . . .	+ 0·798
Mercury (II) . . .	+ 0·793
Copper . . .	+ 0·344
Hydrogen . . .	Zero
Lead . . .	— 0·13
Tin . . .	— 0·14
Nickel . . .	— 0·23
Cadmium . . .	— 0·40
Iron (II) . . .	— 0·44
Zinc . . .	— 0·76
Aluminium . . .	— 1·33
Magnesium . . .	— 1·55

Thus aluminium becomes covered with an oxide film as soon as it is immersed in an aqueous solution, so that a true reading of the metal potential is not obtained. The figures quoted in Table I for aluminium and magnesium have therefore likewise been calculated on a theoretical basis.

It is found as a rule that any metal in the series will displace any more positive metal from a solution of its salts; thus a piece of iron immersed in a solution of a copper salt will precipitate copper from the latter. Furthermore, metals electro-positive to hydrogen do not in general displace hydrogen from acids, whilst those which are electro-negative to this element will do so. The greater the negative electrode potential the more readily will the metal displace hydrogen from acids.

Due to various interfering factors, some of the statements made above do not hold true in all cases. Thus, for instance, it is found that copper is attacked by hot concentrated hydrochloric acid, despite its electro-positive potential to hydrogen. This is probably due to the metal entering the liquid as chlorocuprous acid, $H_2(Cu_2Cl_4)$ which ionises to produce complex anions viz. $(Cu_2Cl_4)^{-}$ and $(CuCl_2)^{-}$. Also copper when exposed to many solutions of salts in the presence of oxygen undergoes rapid corrosion due to "depolarisation" for reasons which will be seen presently.

Electrolytic Cell Formation.—Placing two metals of different potentials in an electrolyte and connecting them together electrically results in a flow of current. Thus a zinc and a copper rod immersed in a dilute solution of sulphuric acid form a simple electrolytic cell. The zinc dissolves, producing zinc sulphate, hydrogen being liberated at the copper. After a short time, however, the current almost ceases to flow owing to the accumulation of hydrogen on the copper surface; this hydrogen is only released very slowly, and results in the “polarisation” of the cell. By putting an oxidising agent in contact with the positive pole it is possible to dispose of the hydrogen accumulation by oxidising it gradually to water. (This is the basis on which the well-known Leclanché cell works, the depolariser in this case being manganese dioxide, which slowly oxidises the liberated hydrogen.)

Thus the rate of oxygen supply either in gaseous form or in the form of an oxidising agent to an immersed or partially immersed metal surface will modify the rate of corrosion.

Differential Aeration.—The effect of oxygen pressure on the corrosion of steel in alkali chloride and other solutions has been investigated.^(3, 4) Oxygen pressures up to twenty-five atmospheres were employed. It was found that when the oxygen pressure was raised from two to five atmospheres prior to immersion of the specimens in sodium chloride solution ($N/2$ or $N/10,000$) or in hard tap water, relatively little corrosion was found in ten days; on the other hand, if the pressure was raised after the immersion of the specimens in the chloride solution, the amount of corrosion increased twenty- or thirty-fold in the same period. When air was substituted for oxygen the amount of corrosion was less than was the case with oxygen at the equivalent partial pressure. With increasing oxygen pressure in these experiments the rate of corrosion was found to increase steadily until a pressure of about twenty atmospheres was reached, after which the rate of increase lessened, perhaps due to agglomeration of the corrosion products which thus would exercise a stifling action on the progress of attack.

These experiments suggest that the effect of increasing the supply of dissolved oxygen may have very varying effects on the rate of corrosion, and exemplify the differential aeration theory of corrosion developed by U. R. Evans,⁽⁵⁾ Bengough and Wormwell⁽⁶⁾ and others partly to explain some of the phenomena of water-line corrosion. The basis of this theory is that a metal tends to be attacked at those areas where the oxygen supply is relatively restricted. Hence this area becomes locally anodic, while areas where the oxygen supply is

greatest become cathodic and are protected. In the case of corrosion of iron by alkali chlorides it is assumed that the oxygen combines with cathodic hydrogen to produce water, whilst the chloride ions combine with the metal forming ferrous chloride; this is, in turn, hydrolysed to ferrous hydroxide, which is gradually oxidised to the ferric state and precipitated in the form of rust (Fig. 2).

Other Factors.—Actually, differential aeration is only one of many effects which play a part in corrosion phenomena. Such irregularities in a metal surface as varying degrees of roughness and differences in physical structure, or non-uniformity in the composition of the

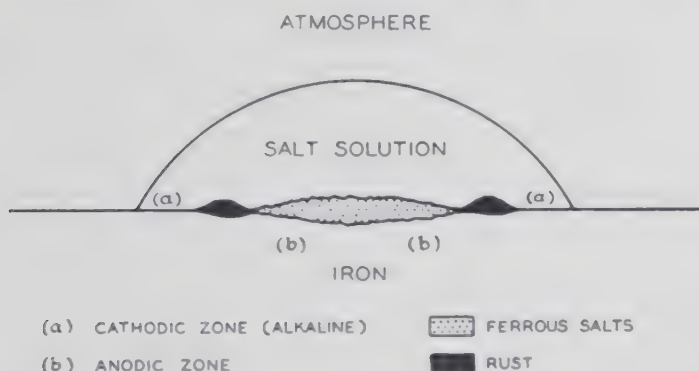


Fig. 2.—Differential aeration. Rusting of iron under a droplet of chloride solution

corroding electrolyte may cause the setting up of potential differences, hence leading to electro-chemical corrosion.

The degree of polarisation which occurs at the electrode surface (either anodic or cathodic) may ultimately determine the rate at which corrosion will occur. Such polarisation can be considerably affected by oxidising agents, as has already been pointed out, while, on the other hand, the products of corrosion, such as metal salts, may accumulate at the surface and shut off the supply of the depolariser, thus reducing the rate of attack. Hydrogen evolution, if it occurs, will also have a similar effect.

Other factors which play an important part in corrosion phenomena are the hydrogen over-potential of the metal, the concentration of various ions (including hydrogen or hydroxyl ions) in the solution and the electrical conductivity of the electrolyte concerned.

Corrosion by Bacterial Action.—Corrosion by bacterial action can be brought about by various means, and such corrosion often plays an important part in the destruction of both ferrous and non-ferrous metals. The bacteria can produce attack by: (a) direct

action, e.g. the production of corrosive substances such as carbon dioxide, hydrogen sulphide, ammonia, organic or inorganic acids; (b) the metabolism of the bacteria producing organic compounds which can act as either depolarisers or catalysts of corrosion reactions; and (c) in cases similar to the anaerobic corrosion of iron, by the action of the sulphate-reducing organisms, where under some conditions the corrosion reaction is an integral part of the metabolic cycle of the bacteria.

Colonies of bacteria can be in direct contact with the metal surface as slimy deposits when they can cause severe localised corrosion not only by the production of corrosive products but by causing differential aeration with the development of local electrolytic cells. Alternatively the corroding medium may be generally infected with the organisms, and if they produce substances which are able to catalyse corrosive reactions, it is possible for the medium to remain abnormally corrosive even after the bacteria have disappeared.

A good deal of investigation has been carried out in recent years on this subject, with special reference to the corrosion of iron pipes and of condenser tubes.

Corrosion Fatigue.—Corrosion phenomena are greatly affected by conditions of stress. Thus, it has been found that if metal specimens are subjected to alternating compression or torsional stresses, for example, in the presence of corrosive agents such as salt solutions, moist air, etc., failure will occur much more rapidly than if similar specimens are submitted to the same cycle of conditions either *in vacuo* or in an inert gas atmosphere. Copper, brass, and mild steel are especially susceptible to corrosion fatigue of this description. Suitable means of protection against corrosion can minimise the liability for the occurrence of such fatigue which may result in sudden and unexpected failures of equipment.

Fractures occurring as a result of corrosion fatigue show a characteristic appearance in the form of narrow surface fissures which taper to sharp, pointed ends. Stress concentration at local notches may play a part in the propagation of fatigue cracks of this type, although they may not necessarily start at such points or even from local corrosion pits due to normal stressless corrosion phenomena.

The chemistry of corrosion has been the subject of much investigation.⁽⁷⁾ It is not feasible to deal adequately with the fundamental theory of the subject here, although the data available (both theoretical and practical) will be referred to from time to time so far as they affect the application of our knowledge of the subject to the principles and practice of metal finishing.

In the ensuing pages some account will be given of the characteristic properties under corroding conditions of a number of metals most commonly made use of in industry.

IRON AND STEEL

As is well known, ordinary iron rusts rapidly when exposed to the atmosphere, especially at temperatures below the dew-point. Rusting does, however, occur on clean iron even in an atmosphere of low humidity; the attack commences at isolated centres sporadically distributed over the metal surface. These points are generally places where there are inclusions in the metal surface or where variations in the physical or crystalline structure of the metal occur.

Homer, quoted by Hudson,⁽⁸⁾ has shown that under conditions of immersion in a variety of solutions rusting generally commences on steel surfaces at places where there are sulphide inclusions or at particles of rolled-in scale. Not all sulphide inclusions act as centres of corrosion, however, but the evidence is in favour of the view that sulphide segregation is conducive to the initiation of rusting on steel surfaces. On the other hand, siliceous or aluminous inclusions did not act as centres for the commencement of rusting.

Once rusting has started corrosion is first accelerated, then slowed down and finally proceeds at a fairly steady rate, owing to the gradual extension of the rust foci, until the entire surface is covered with a thin rusted layer.⁽⁹⁾ The initial extension of the rusted areas represents the period of accelerated attack, with a subsequent slow decrease in the rate of corrosion as the boundary lines which separate the rusty from the clean areas gradually decrease in length. Subsequently, when the entire surface is covered, further corrosion can only proceed through the rust coating into the depth of steel. Such rusting usually proceeds at a relatively constant speed, since rust as formed under normal atmospheric conditions is highly permeable to air and moisture, and exercises little protective effect on the underlying metal surface.

Influence of Dust on Rusting.—The work of Vernon⁽¹⁰⁾ has shown the importance of dust in the promotion of the rusting of iron. It was found that iron specimens exposed at temperatures above the dew-point under a muslin screen showed no rusting over prolonged periods. A piece of iron after exposure indoors behind muslin for eleven months appeared quite clean; on subsequent exposure to normal conditions without protection rusting commenced, but even then the onset of attack was much slower than in the case of a similar specimen freshly cleaned and exposed. Thus

a protective film had formed on the metal surface and continued to protect the underlying metal to a degree from further attack.

Vernon classified the types of dust particles to the effects of which exposed steel can be subjected as follows:

- (i) Intrinsically active particles, e.g. ammonium sulphate.
- (ii) Intrinsically neutral particles, e.g. silica.
- (iii) Indirectly active particles, e.g. charcoal, which can adsorb corrosive gases, such as sulphur dioxide, and bring about a high concentration of the corrosive agent at local points on the metal surface in unsaturated atmospheres.

Where super-saturated conditions prevail, ammonium sulphate particles accelerate attack greatly, provided the atmosphere is pure; in the presence of sulphur dioxide the influence of the ammonium sulphate particles is masked. In an unsaturated atmosphere the influence of the ammonium sulphate particles is considered additive to that of the sulphur dioxide.

Passive Films.—The effects of protective films have been the subject of much investigation, both on ferrous and non-ferrous metals. In particular, films produced artificially by heating or by "passivation" in strong nitric acid have been examined. It is well known that iron, when immersed in concentrated nitric acid (and in other oxidising agents), is no longer capable of being dissolved in the dilute acid, and will not precipitate copper or silver from solutions of their salts. This effect is believed to be due to the presence of a thin oxide film on the metal surface. When this theory was first put forward objections were raised to it, among other reasons, on the obvious count that the oxide of iron should normally be soluble in dilute acids, and also because of the fact that no distinction could be found between the reflecting properties of passivated and non-passivated iron mirrors. The work of Hedges⁽¹¹⁾ showed that ferric oxide, when anhydrous, is not dissolved by nitric acid until a temperature of about 75° C. is reached, when small gas bubbles appear. It was then found that when electrolytic iron was passivated in nitric acid and the temperature of the acid was gradually raised, the temperatures at which reaction between acid and metal commenced followed the corresponding temperatures obtained with powdered ferric oxide almost exactly. Furthermore, the nature of the reaction in both cases was closely parallel.

The amount of oxide dissolved in each case was quite small, since ferric oxide dissolves in acids with great difficulty, especially when

freshly ignited and free from water. It is to be expected that a passive film produced in concentrated nitric acid would likewise be free from water. It is of interest to note that the attack of the nitric acid on passivated iron at 75°C . shows a characteristic periodicity, in that attack commences and diminishes at fairly regular intervals of a few seconds' duration, and remarkable effects showing the transmission of waves of passivity along iron wires have been produced. The results obtained have caused much speculation, and analogies have been drawn between them and the transmission of impulses along nerves in biological phenomena.⁽¹²⁾ Actually, passive iron does dissolve extremely slowly in concentrated nitric acid due to the gradual dissolution of the oxide. This accounts for the apparent disappearance of passivity at higher temperatures. Passivated iron also dissolves in hydrochloric acid, since in this case the ferric oxide is reduced by the latter acid to ferrous oxide, which is very rapidly attacked by the acid.

Evans⁽¹³⁾ has isolated the passivating films produced on iron, both by chemical oxidising agents (such as potassium dichromate) and by heat. This was done by treatment with iodine, which attacks the boundary between metal and oxide preferentially. The reagent has no action on the oxide, which can then be flaked off. He did not find it practical to isolate the nitric acid film, because the latter tends to break down on removal from the acid. Under the microscope, these films are shown to consist of the actual surface film of the metal, and copy the contour of the specimens, including surface ridges and grooves. The flakes obtained are extremely fine, transparent, and of varying colours.

More recently Gulbransen⁽¹⁴⁾ by using a vacuum microbalance technique has succeeded in measuring the thicknesses of the oxide films on iron, stainless steels, and chromium iron. In the case of iron passivated in nitric acid, the film weight was found to be of the order of 1.1×10^{-6} gm./cm.² (78 Å.), whilst a film produced in air was examined and weighed 0.44×10^{-6} gm./cm.² (29 Å.). The films possessed remarkable stability, and were in fact stable at as low as 10^{-6} atmosphere oxygen pressure, whilst in vacuum (5×10^{-6} mm. mercury) they retained their stability at 600°C .

Protective films play an important part in corrosion phenomena, and are fundamentally responsible for the corrosion resistance of such intrinsically oxidisable metals as chromium; they are also responsible for the special corrosion-resisting qualities of the stainless steels.

Copper-bearing Steel.—The presence of small percentages of

copper in steel (0.2 to 0.5 per cent) appears to increase its corrosion resistance by 15 to 20 per cent, the most marked improvement being shown in industrial atmospheres. The effect is most readily demonstrable in the low carbon range of steels. The introduction of copper seems to have little influence on the physical properties of the metal. Such effects as have been noticed are a slight lowering of the ductility and impact value with a possible increase in the tensile strength and the yield-point. The copper has been stated to exercise its function by fixing sulphur particles in the form of the relatively stable copper sulphide.⁽¹⁵⁾ Under acid conditions an adherent copper film appears to form on copper-bearing steels which may gradually oxidise. Generally speaking, rust films on this type of steel are dark in colour and much finer and more adherent than on similar non-copper-bearing steels; there is also less deep local pitting corrosion, although the rust may be more widely spread over the metal.

Wrought Iron.—Wrought iron exhibits on occasion exceptionally low rates of corrosion. Below the outer scale, which is generally although not always of a flaky type, there is often a very tightly adhering layer of scale which is highly protective. On the other hand, Lewis and Evans⁽¹⁶⁾ have found that even when descaled completely, wrought iron shows rather better corrosion resistance than mild steel on prolonged exposure tests.

One characteristic feature of corrosion phenomena in wrought iron of some types is a tendency for corrosion to spread laterally rather than vertically within a section of the material due to the influence of the thin slag laminae which are often formed in wrought-iron sheet during the rolling stage of its production. Wrought iron has an exceptionally low manganese and carbon content, and this probably also plays a part in reducing its liability to corrosion.

Cast Iron.—Cast iron shows good corrosion resistance and forms relatively adherent rust films as a rule on exposure; graphite flakes appear to act as cathodic areas, but their presence also helps in that they form a network for holding corrosion products in close proximity to the metal surface thereby stifling further attacks. A fine grain in cast iron is conducive to good resistance; large graphite flakes are undesirable, especially if they extend from the surface into the interior of the metal, since corrosion products may form along the graphite flakes, and by their expansion split up the metal surface.

Stainless Steels. There are numerous stainless steels which have different degrees of resistance to a variety of conditions. They do not generally come into the field of metal finishing so far as protective coatings go, but the pickling and polishing of all types of

stainless steel is of great importance if the maximum resistance to corrosion is to be obtained. Thus particles of rolled-in scale or other foreign matter may act as foci for attack, and a smooth high finish is therefore essential for maximum service. The corrosion resistance of the stainless steels is due to the presence of an extremely thin protective oxide film, and any discontinuity which prevents the formation of a complete film or impairs its ability to re-form itself when damaged reduces the corrosion-resisting qualities of the steel considerably.

Chromium is the fundamental ingredient of stainless steels which is responsible for the development of the self-healing passive oxide film, but the addition of metals such as nickel and molybdenum may modify the properties of the steel so far as particular corroding media are concerned. It is of interest to note that in some cases where a grade of stainless steel is attacked by a corroding medium, resistance to the latter may be acquired by first attacking the steel in the medium, washing and then allowing it to stand before re-submitting it to contact with the same medium. Apparently a protective film is able to form as a result of this treatment which has a high degree of resistance to the material concerned.

On the other hand, there are often certain substances which reduce the corrosion resistance of stainless steels to particular corrosive agents by "activating" them. Thus a chloride solution becomes much more corrosive to stainless steels which are otherwise resistant when a small amount of acid is present. In the same way the presence of small quantities of sulphuric acid increases the rate of attack of the steel by citric acid.

Other Problems.—It is only possible here to mention in passing other important problems involving the corrosion of iron and steel. The attack on ships' hulls and steel piers by sea-water, the destruction of buried pipes and pipe-lines due to soil corrosion and stray electric currents, and many other phenomena, have been the subject of a great deal of attention, and the failures due to them have been immensely reduced by effective measures adopted for their prevention.

COPPER

The corrosion of copper is to a considerable extent affected by the presence or relative absence of traces of sulphur compounds in the atmosphere. Air which is free from sulphur compounds has no tarnishing effect on the metal. Thus, when the concentration of reactive sulphur corresponds to about one volume of hydrogen sulphide in 35 million volumes of air (a condition approximating to

town air in winter) tarnishing of copper is comparatively rapid, and results in a purplish surface being produced on the metal in the course of a week or two. Tarnishing ceases when the concentration of reactive sulphur falls below one volume in 600 million volumes of air (a condition approximating to suburban atmospheres during summer).⁽¹⁷⁾ On the other hand it is found that the tarnish film contains only 6 to 9 per cent of sulphide, the rest being assumed to be oxide.

On further exposure to the atmosphere the film thickens, due to the action of oxygen on the copper sulphide. When moisture is absent the attack of air containing sulphur dioxide is small. There appears to be a critical relative humidity at 63 to 75 per cent, below which there is only slight darkening of the copper and little attack, even when the sulphur concentration is fairly high.⁽¹⁸⁾

Vernon also investigated protective oxide films formed on copper surfaces.⁽¹⁹⁾ By heating for about an hour at temperatures as low as 75° to 100° C. an invisible film is produced on copper sheets which inhibits tarnishing when the metal is subsequently exposed to the atmosphere even in the presence of traces of sulphur. A similar invisible protective film could be produced by exposing copper to a comparatively clean atmosphere for a period of about a month; subsequent exposure to a typical industrial atmosphere showed that the copper was relatively resistant to tarnish. When the copper is exposed to sulphur-containing atmospheres the mixed film of oxide and sulphide is very permeable to moisture and oxygen, so that such a film exercises little protective effect. Pure sulphide films behave similarly.

Corrosion Products.—Analyses carried out on the green patina from old copper roofs have shown that they consist largely of basic copper sulphate and a certain amount of basic copper carbonate.⁽²⁰⁾ It seems likely that the sulphide is the first product of corrosion, part of which is gradually converted by rain containing dissolved carbon dioxide into carbonate, the rest being oxidised to basic sulphate. In marine atmospheres a certain amount of chloride is always present, but this is generally exceeded in amount by the sulphate. In town atmospheres the green colour only develops after a preliminary black stage. It is interesting to note that the final green product has the composition $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$ corresponding with that of the mineral brochantite. The film produced is often extremely tenacious and adherent, which accounts for the long life of some copper roofs extending into hundreds of years. When the deposit is removed the metal beneath is often found to be remarkably free from pitting.

ZINC

Zinc and zinc-base alloys are chiefly affected by the acid content of the atmosphere. The corrosive effect of moisture is increased considerably when the water contains appreciable quantities of dissolved carbon dioxide. The oxide film is very porous and granular in nature, and exercises little protective effect on the underlying

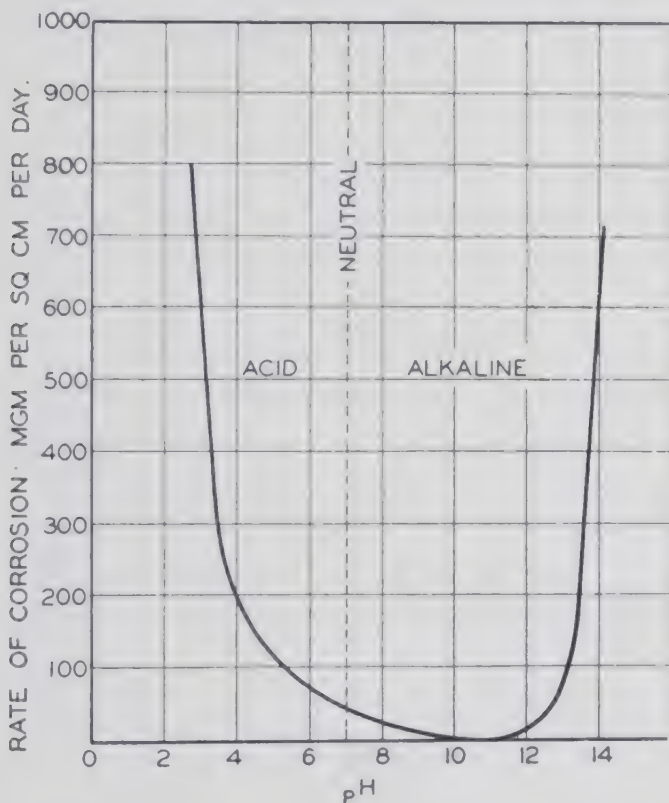


Fig. 3.—Rate of corrosion of zinc at different pH values

metal; oxygen diffuses readily through it. Zinc corrodes very slowly under neutral conditions, as has been shown by experiments carried out in sodium chloride solutions made alkaline and acid by sodium hydroxide and hydrochloric acid respectively.⁽²¹⁾ (Fig. 3.) Very marked increases in the rate of corrosion are found as the pH rises or falls from a limiting range of pH 10 to pH 12. Within this range the rate of corrosion is small. As the conditions become more acid or alkaline the protective oxide or hydroxide films are dissolved by the liquid medium. Zinc is very susceptible to water-line corrosion owing to the solubility of the hydroxide (formed from

TABLE II
NOMINAL COMPOSITIONS OF ZINC ALLOYS

Alloy	Mazak 3, per cent	Mazak 5, per cent
Aluminium	4·1	4·1
Copper	—	1·0
Magnesium	0·04	0·03
Iron (max.)	0·075	0·075
Lead (max.)	0·003	0·003
Cadmium (max.)	0·003	0·003
Tin (max.)	0·001	0·001
Zinc	Remainder	Remainder

TABLE III
DATA FROM EXPOSURE OF DIE-CASTING ALLOYS

Material	Corrosion penetration: in. per 10 years	
	Palmerton, Penn.	New York City
Rolled zinc	0·00023	0·0017
Galvanised iron	0·00016	0·00099
Zamak 3	0·00026	0·0012
Zamak 5	0·00016	0·00099

the oxide) which exercises a degree of protection temporarily. Corrosion of zinc sheet in salt solutions under some conditions is often laminar in nature, the corrosion products tending to destroy layers parallel or almost parallel to the metal surface. The metal then becomes very weak and will crack when subjected to any degree of bending.

Die-casting Alloys.—Zinc alloys for die-casting are now very closely controlled in composition, since the presence of excessive quantities of impurities leads to rapid intergranular corrosion and breakdown. This corrosion takes place along the grain boundaries, and results in the distortion and eventual failure of the entire casting; in some cases selective network attack can occur in the eutectic areas. It has been found that excessive amounts of lead and tin in particular are likely to increase the rate of attack by moist atmospheres on

zinc-base die-casting alloys; the cadmium and iron must also be closely controlled. In atmospheres containing salt or in acid solutions copper and nickel promote corrosion.

Various alloy compositions have been used for die-casting, but two are at present in most general commercial use. They are known as the "Mazak" Alloys (or "Zamak" in the U.S.A.). Mazak 3 is used for its good impact strength and where the retention of dimensional accuracy is important; Mazak 5 has good resistance to corrosion. Table II shows the nominal compositions of the alloys.

When the die-casting alloys are within specification the corrosion resistance and behaviour under corroding conditions are similar to those obtained with rolled zinc sheet and with galvanised iron. Some data obtained during a ten-year exposure test in the U.S.A. are shown in Table III. This table also gives some indication of the relative corrosion resistance of the different die-casting alloys.⁽²²⁾

BRASS

Brass represents a typical case of the corrosion of alloys. Generally speaking, the brasses have a reasonable degree of resistance to corrosion, and there is some evidence that they are capable of forming a protective oxide film over their surface; whilst these films are not so adherent or non-porous as those formed on copper they are of better value from this point of view than the zinc oxide films. In industrial atmospheres the 70 : 30 brasses are less resistant than lead, commercial aluminium, or the tin and aluminium bronzes, but more so than nickel, commercial zinc, and duralumin. In marine atmospheres the brasses prove somewhat superior to commercial zinc, tin, commercial aluminium and duralumin, and inferior to lead, nickel, and the bronzes.⁽²³⁾ Fig. 4 shows the relative rates of corrosion of some non-ferrous metals on exposure to weather.

Condenser Tube Corrosion. A special brass corrosion problem is that connected with the attack of water on brass condenser tubes. Although condenser tubes were formerly made mainly of an alpha-brass containing 70 per cent copper and 30 per cent zinc, Muntz metal (an alpha-beta brass containing 60 per cent of copper and 40 per cent of zinc) has also been employed for some purposes. It is to be expected that the latter brasses containing two crystalline forms might also not withstand corrosive conditions too well, since it is likely that electro-chemical potentials would arise between the two kinds of crystals. Sometimes when the protective film has been able to establish itself good service is obtained from alpha-beta brasses, but when corrosion starts the beta crystals appear to become anodic,

so that they are soon replaced by a porous copper mass; the brass then becomes extremely weak. This re-deposition of copper is discussed below. Admiralty brass makes use of a 1 per cent content of tin to increase the corrosion resistance, which it does to some extent.

It is often found that the corrosion products of brass contain a porous deposit of metallic copper in addition to zinc compounds, such as basic zinc chloride. This type of corrosion therefore became known as "dezincification," since it was thought that the copper was the residue left after the zinc had corroded away. Bengough and

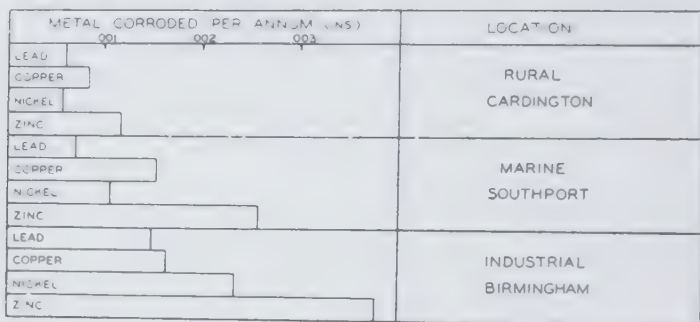


Fig. 4.—Relative rates of corrosion of non-ferrous metals exposed to the atmosphere. (Hudson)

May,⁽²⁴⁾ however, showed that the copper is actually re-deposited metal. The initial products of corrosion are copper and zinc compounds; the copper corrosion products then attack a further amount of brass, so that mainly zinc derivatives are left in the final corrosion deposit; pits produced by the attack on the brass may be filled with a plug of porous copper, or sometimes the brass surface may be covered by a layer of re-deposited copper. Arsenic plays an important part in the phenomenon, and brasses containing more than 0.01 per cent of arsenic do not show dezincification; manganese and iron tend to promote dezincification, whilst, on the other hand, tin, nickel, aluminium, tungsten, and lead have an inhibiting effect.

Aluminium brasses are now almost exclusively used for condenser tubes, the aluminium content of the brass being of the order of 2 per cent, whilst copper-nickel alloy tubes containing about 30 per cent of nickel have been installed by the Admiralty, and have given satisfactory results.

Season Cracking.—Brass is liable to a characteristic form of

corrosive attack known as season cracking. It is confined to brasses which are in a state of stress, usually as a result of cold working. In order that season cracking may develop in the atmosphere the presence of traces of ammonia is necessary; the ammonia content of the atmosphere quite commonly reaches the low concentrations needed for season cracking to manifest itself. The ammonia results in the brass being attacked along the grain boundaries for some reason which is not clear, so that the component cracks and may even disintegrate. Salts of mercury are extremely active agents in developing intergranular corrosion in stressed brass, and immersion in mercurous nitrate solution constitutes a standard test for the liability of cold-worked brass to this type of attack. A suitable annealing treatment will often remove the internal stresses liable to produce conditions favourable to season cracking without appreciably reducing the hardness of the brass.

Brass is readily attacked by nitrous fumes with the formation of green hygroscopic corrosion products; such attack is liable to occur in electrical equipment (especially where high-tension spark discharge occurs), and constitutes a source of failure in such equipment, particularly when used under unfavourable conditions. Attack by nitric and nitrous acids is, however, dependent on the presence of moisture, and under relatively dry conditions such corrosion is not likely to become serious.

Bronzes, containing tin, are very much less liable to corrosion than brass under practically all conditions.

ALUMINIUM AND ITS ALLOYS

Pure aluminium is, generally speaking, more corrosion-resisting than its alloys. The heat-treatable alloys characterised by duralumin (containing 4 per cent copper, 0.5 per cent manganese, and 0.5 per cent magnesium) are the strongest mechanically, but have a relatively lower resistance to corrosion. After corrosion has proceeded to some extent, however, further attack ceases, due to the self-stilling effect of the oxide film which forms on the surface.⁽²⁵⁾ In "Alclad" the intrinsic corrodibility of duralumin is overcome by coating the latter with pure aluminium by rolling composite sheets of the two metals. The corrosion of duralumin is greatly accelerated by incorrect heat-treatment, such as delayed quenching or quenching in water at too high a temperature. Intergranular attack may then occur under suitable conditions, perhaps due to the corrosion of the particles of CuAl_2 , which are preferentially precipitated at the grain boundaries in these circumstances (Fig. 5).

Intergranular attack is also more likely to occur in marine atmospheres, especially in tropical climates.⁽²⁶⁾

Wrought alloys containing manganese (about 1 per cent) are amongst the most corrosion-resisting alloys of this class. Alloys containing appreciable amounts of magnesium (in proportions up to 10 per cent) are highly corrosion resistant. Thus Birmabright, containing 3.6 per cent of magnesium and 0.75 per cent of manganese (max.), combines corrosion resistance to marine atmospheres with

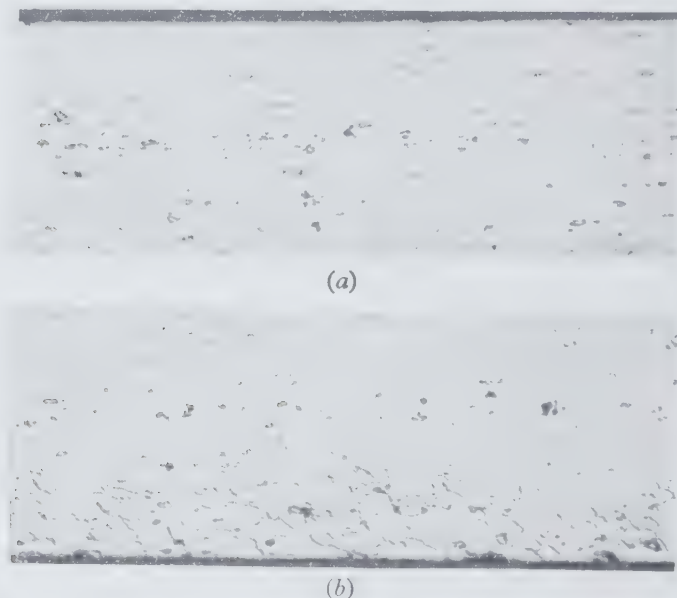


Fig. 5.--Intergranular corrosion of Duralumin. Section of Duralumin sheet after weathering
(a) Heated to 500°C. and quenched in water (showing normal structure). ($\times 100$)
(b) Heated to 500°C. and cooled in air (showing intergranular corrosion). ($\times 100$)

structural strength. Of the casting alloys those containing silicon (5 per cent or 13 per cent) are the most satisfactory. Generally speaking, the cast alloys are not subject to intergranular corrosion.

Aluminium itself is a very reactive metal, and its relatively high resistance to corrosion is due to the presence of an invisible and comparatively impervious oxide film on the metal surface. If this film is damaged or dissolved by corrosive agents such as acids, alkalis, or salts, corrosion proceeds apace.

Types of Corrosion.—The corrosion of aluminium and its alloys manifests itself often in the form of local pitting, which may be due to differential aeration effected by the presence of traces of grease,

dust, or by surface defects or inclusions; these tend to cause the breakdown of the protective oxide film. Local potential differences may also be set up between areas on which the oxide film has built up to different thicknesses.⁽²⁷⁾ Corrosion results in a considerable loss of fatigue strength on the part of aluminium alloys. Thus, in one series of experiments, duralumin immersed in tap-water for twenty-four hours had its fatigue strength reduced by some 25 per cent.

Marine atmospheres and chlorides are especially prone to set up corrosion of aluminium and its alloys. Sea-water, if it comes into contact with light alloys, is highly destructive, although the magnesium-containing alloys and the silicon-containing casting alloys are more resistant than others. A summarised account of the results obtained by investigators who have conducted sea-water exposure tests on aluminium and its alloys is given by McKay and Worthington.⁽²⁸⁾

Aluminium withstands some acid solutions very well; thus it resists the action of concentrated nitric acid and all strengths of acetic acid. In the absence of chlorides the rate of attack appears to depend largely on the hydrogen ion concentration produced by the acid concerned.

TABLE IV
ATTACK OF ALKALIS ON ALUMINIUM

Exposure for 30 mins.	Loss in weight, mgm. per sq. dm. per day	
	Without silicate	With silicate
10 per cent NaOH at 68° F. . .	15,000	17,000
10 per cent Na ₂ CO ₃ at 149° F. .	4,600	5

In alkaline solutions, on the other hand, aluminium alloys are readily attacked, due to the solubility of the oxide in alkalis; ammonia solutions behave exceptionally, however, and are generally resisted fairly well. Sodium silicate reduces the rate of attack by sodium carbonate considerably. Thus, Röhrig⁽²⁹⁾ showed that the addition of only 0.75 per cent sodium silicate had a profound effect on the rate of attack of sodium carbonate on pure aluminium sheet, but had no inhibiting influence on caustic soda solutions (Table IV).

The addition of chromate has a similar action in inhibiting the action of alkalis on aluminium.

MAGNESIUM AND ITS ALLOYS

Magnesium alloys are subject to both pitting and stress corrosion. Generally speaking, they are readily attacked by acids, but are highly resistant to alkalis. Intergranular corrosion in the commercial alloys is less often found, although when it does occur the crystal structure plays a considerable part in the liability of the metal to attack.⁽³⁰⁾ On exposure, the magnesium alloys become covered with a greyish film of oxide which is subsequently attacked by the carbonic and sulphurous acid content of the atmosphere with the formation of magnesium carbonates and sulphates, the former predominating in amount.⁽³¹⁾

Chlorides of all types are extremely active in promoting corrosion of magnesium, whilst most other salts have comparatively little effect. The attack of magnesium by chlorides has been investigated by Whitby;⁽³²⁾ it was found that the action of sodium chloride solutions shows itself in the form of hydrogen evolution from the metal surface at isolated points which gradually diminish in number. The unattacked areas slowly become covered with a brownish-yellow film and a loose layer of magnesium oxide.

Fluxes.—Chloride fluxes are widely used in the production of wrought magnesium alloys and in the manufacture of castings, with or without other additions such as fluorides. Their object is to prevent the formation of oxide and nitride inclusions in the metal which would have a very adverse effect on its mechanical properties. In the circumstances, chloride residues may be left in the metal unless due care is taken, and if these are near the surface, or are exposed during machining operations, the salts will react in the presence of the moisture in the atmosphere with the formation of the very hygroscopic magnesium chloride; this will expand in the pores of the metal and cause rapid corrosion and disintegration of the surface.

Alloying Elements.—Local iron inclusions in magnesium facilitate pitting attack. Iron is insoluble in magnesium and becomes dispersed in the alloy, the particles acting as centres for the initiation of electrochemical corrosion. The inclusion of manganese in commercial magnesium alloys is therefore practised, one of the best of the corrosion-resisting alloys being the binary alloy containing approximately 2 per cent of manganese. The manganese dissolves in the magnesium to some extent, and when the alloy is maintained just above the melting-point for a period the iron is precipitated from the melt together with the excess of primary crystallising manganese.

This alloy on exposure to marine atmospheres develops a greyish-brown protective film which appears to consist of a mixed hydroxide of magnesium and manganese which is very adherent. Aluminium also reduces the solubility of manganese, so that by making use of the ternary alloy containing both these added elements the corrosion resistance is again improved, whilst the mechanical properties are favourably affected at the same time. The types of alloys used in present-day industrial practice are exemplified in Table V, which shows the nominal compositions of some commonly used magnesium alloys.

TABLE V
TYPES OF MAGNESIUM ALLOYS IN CURRENT USE

Commercial designation	Form	Composition (per cent)				Miscellaneous
		Al	Zn	Mn	Mg	
Elektron A8	Cast	8.0	0.25-1.0	0.3	Bal.	
„ AM503	Sheet and cast	0.2	0.2 (max.)	2.5 (max.)	Bal.	Cu 0.2 (max.) Si 0.4 (max.) Impurities 0.5 (max.)
„ AZ91	Die-cast	9.7	0.6	0.3	Bal.	
„ AZM	Forgings	6.3	1.0	0.3	Bal.	
„ AZG	Cast	6.0	3.0	0.3	Bal.	

Many other alloying elements have been introduced into magnesium, but on the whole they do not have a favourable influence on the corrosion resistance of the metal. The addition of small percentages of cerium has been proposed to improve corrosion resistance and also to improve the strength of magnesium alloys at elevated temperatures.⁽³³⁾

The corrosion resistance of magnesium alloys is increased by heat-treatment, when a homogenised structure is obtained. Precipitation heat-treatment appears to lessen the resistance to corrosion.

Stress corrosion shows itself chiefly in the magnesium alloys containing high percentages of alloying constituents. Other alloys, such as Elektron AM503, for example, are not affected, and it has therefore been proposed that those compositions liable to stress corrosion should be clad with an insensitive alloy.

LEAD

Lead is a metal of remarkable stability under conditions of atmospheric exposure, and its resistance to water is also good, especially when the latter is relatively hard. This accounts for its successful use in water-pipes, as any degree of solubility of poisonous lead compounds in drinking water would be very undesirable.

The presence of sulphates and bicarbonates in the water results in the formation of a highly adherent film of basic lead carbonate on local anodic parts of the metal, with a corresponding deposit of insoluble calcium carbonate on the cathodic portions. The latter deposit effectively protects the lead from further attack.

Soft waters, especially those from peaty areas which contain organic acids, are more capable of dissolving the metal, the insoluble protective film not being readily formed in such cases. The artificial addition of carbonate to the water in localities where the water is very soft is sometimes practised.

Lead resists sulphuric acid extremely well, and finds application in chemical plant where resistance to the acid is required.

TIN

Tin has the property of resisting atmospheric corrosion extremely well, whilst it also withstands the corrosive action of many foodstuffs. This latter characteristic, coupled with its non-toxicity, accounts for its widespread use in the canning industry as a coating for cans and food-containing utensils. Tin is seldom used in the massive form, but is generally employed as a coating metal on steel or on non-ferrous alloys. It may be applied either by dipping the basis metal into the molten tin or electrolytically.

In the absence of air, tin is particularly corrosion-resistant owing to polarisation by hydrogen.

NICKEL

Nickel is usually employed as a protective electro-deposit, generally as an undercoat for chromium. Nickel deposits are applied to brass, steel, copper, zinc-base alloys, etc., but when failure occurs this is due largely to the corrosion of the basis metal through pores or discontinuities in the coating metal and not to the corrosion of the nickel itself.

On exposure to the atmosphere nickel develops a tarnish, and under highly humid conditions a thick yellowish film is formed which can

only be removed by vigorous rubbing. If this film is allowed to remain in contact with the metal the rate at which further corrosion takes place is increased.

The formation of this film is induced by condensation, since if the metal is kept at temperatures above the dew-point it remains bright. The dew-point need not actually be reached, however, 70 per cent saturation being sufficient for such filming to occur.

Sulphur compounds play an important part in the fogging of nickel, since the film consists essentially of a basic sulphate of the metal.

At low humidities nickel tarnishes. This phenomenon differs from fogging in that the discoloration is brownish in colour and consists of an oxysulphide of nickel.

CONTACT CORROSION

When two metals are in contact it is often found that a greater degree of corrosion occurs at the point of contact than over the general surface of the metal. Similarly, increased corrosion is also often found when metals are in contact with non-metallic substances such as glass or bakelite.⁽³⁴⁾ In view of the fact that many engineering assemblies nowadays contain quite a considerable number of metallic contacts of this kind it is evident that the problem of contact corrosion warrants careful attention.

Contact corrosion might be more properly termed "crevice corrosion", and the familiar phenomena of differential aeration occur due to the absence of free access of oxygen at such points with the result that there is more likelihood of attack of the metal surfaces within the crevice. Electro-chemical effects come into play, especially when the metals are relatively far apart in the electro-chemical series. In each crevice a minute electro-chemical cell is formed, the electrolyte consisting of condensed moisture containing traces of dissolved gases such as carbon dioxide, sulphur dioxide, and ammonia.

Magnesium-base alloys are amongst the metals most susceptible to contact corrosion. The magnesium behaves anodically, and is itself attacked first in the event of contact corrosion occurring. Aluminium and its alloys should on no account be coupled with magnesium. When such contacts are essential a chromate inhibiting primer should be applied to the contacting surfaces. When magnesium is put into contact with various metals in a 3 per cent solution of sodium chloride their effect in order of decreasing liability to attack of the magnesium is as follows: Platinum, aluminium, iron, nickel, copper, lead, manganese, zinc, mercury.⁽³⁵⁾

Steel in contact with brasses or bronzes is undesirable, since

copper salts are liable to dissolve under suitable conditions, with the result that spongy copper will be deposited on the steel. Hence local corrosion cells will be set up stimulating further attack.

In contact with zinc or cadmium (metals which behave anodically towards iron and steel) the former metals suffer increased corrosion whilst the latter are protected in moist atmospheres. With metals cathodic to iron (e.g. copper, nickel, silver, and gold) the iron is attacked, especially under conditions of high relative humidity. Hippensteel⁽³⁶⁾ found that corrosion of iron is accelerated by contact with copper and nickel in marine atmospheres and not by tin, but in industrial atmospheres tin and nickel are predominating accelerators. It is of interest to note that in the case of steel covered with mill-scale the latter acts cathodically, and is capable of bringing about increased attack.

Zinc, standing between aluminium and iron in the electro-potential series, is generally anodic to iron, nickel, lead, tin, copper, cobalt, and their alloys. When zinc and aluminium are coupled there is practically no acceleration in the corrosion of either; the zinc, if anything, tends to be cathodic. The contact corrosion of steel and aluminium can be almost completely eliminated by anodising the aluminium and zinc plating the steel.

Hippensteel has listed the combinations of metals in which there was no change in the normal corrosion rate of the single metal by contact with a second metal. The couples tested were all possible combinations of zinc, aluminium, iron, lead, tin, nickel, and copper.

On a basis of these tests the general conclusions reached were:

- (a) The metals tend to accelerate the corrosion of other metals with which they are coupled in roughly the following order: Nickel, tin, copper, iron, lead, aluminium. The rating was arrived at by counting the number of times each metal appears as an accelerating agent in the comprehensive series of test specimens exposed during the investigation. This indicates that copper, nickel, and tin are most prone to cause difficulty when coupled with other metals.
- (b) The metals may be rated from best to worst, according to their susceptibility to acceleration of corrosion by galvanic action as follows: Nickel, copper, tin, lead, aluminium, zinc, iron.

This information is of value in selecting electro-plated finishes on washers or other parts which have to come into contact with different metals.

Little has been published on contact corrosion of commercially used alloys apart from the work of LaQue and Cox, who prepared a galvanic series of many industrial alloys in sea-water.⁽³⁷⁾

Conclusion.—This survey of some of the metals employed in industry and with which finishing processes are concerned can only concern itself with generalities. In the succeeding chapters detailed consideration of the properties of these metals and their behaviour when applied as electro-deposits will be studied.

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CHAPTER II

DESCALING AND PICKLING PROCESSES

The general term of "scale" is applied to the oxide coatings which develop on metals when they are exposed to elevated temperatures. Scale can form during a variety of operations, e.g. in casting, forging, hot rolling, and annealing.

The composition and the physical structure of the scale depends on the conditions under which it is formed. Thus, such factors as the temperature and duration of heating, the mechanical effects of rolling, forging, etc., the composition of the furnace atmosphere, and the duration of the cooling cycle, all influence the type of scale which is produced. Before almost any finish can be applied to metals, this scale must be removed. Sometimes painting is carried out on top of scale, but this is not to be recommended. In addition, the removal of scale is carried out between pressing and drawing operations to eliminate the heavy wear of tools and dies which would take place were an attempt made to work scaled metal.

Much investigatory work has been carried out on the structure of scale on metals, and this will be referred to later, since the structure of the scale has a profound effect on descaling by pickling.

BLAST-CLEANING ⁽¹⁾

The removal of scale from surfaces by projecting abrasive particles at high speed on to them is a convenient method, and is commonly used for a variety of articles. Moreover, the successful use of this method does not depend on the chemical nature of the scale, and can be applied equally well to scale formed under all conditions; naturally, however, harder or more ingrained types of scale take somewhat longer to remove and may involve the use of different sizes and types of abrasive.

The process is especially suited for the removal of siliceous scales produced in welding or sand-casting; these are strongly resistant to acids and blast-cleaning presents a satisfactory method of dealing with this type of scale. Care must be exercised in the case of rolling scales, however, to avoid driving particles into the metal surface, as these may then act as centres for corrosion when subsequent finishing coatings have been applied. In the best present-day practice the

operation is carried out in two main types of plant: (a) pressure-operated, and (b) centrifugal.

Pressure Plant.—Here the abrasive is passed from a hopper to a closed chamber, into which air at high pressure is blown. The air picks up the abrasive grains (usually sand or steel grit) and then passes into a hose and thence to a nozzle. The compressed air carrying the abrasive particles is directed on to the surface to be cleaned by means of the nozzle (which may be fixed or movable), and the operation is continued until the scale is removed. This is usually accomplished very quickly.

In order to enable the plant to function continuously, an intermediate chamber should be provided between the hopper and the pressure chamber. While the plant is in operation the valve between the pressure and the intermediate chamber is left closed, and that between the latter and the hopper is open. Thus, the abrasive is collected in the intermediate chamber, and when the supply in the pressure chamber is exhausted the valve connecting the two latter compartments is opened; the air is then admitted to the intermediate chamber, automatically closing the hopper valve. The abrasive passes into the pressure chamber, and after closing the valve leading to the latter, blasting can be continued. The abrasive is returned to the hopper periodically and must be sieved from time to time to remove dust derived from both worn abrasive and the surface being cleaned. The abrasive can be directed on to the parts being cleaned either by hand operation through apertures in the plant or by manipulating the parts to be cleaned under fixed nozzles. Fig. 6 shows a shot-blasting room provided with a hand-operated rotating table placed half in and half out of one side of the room, enabling fresh work to be loaded outside whilst the operator deals with work on the portion of the table inside the room.

For dealing with small castings, forgings, etc., the barrel type of unit is satisfactory; in this the parts are turned slowly in a cylindrical perforated barrel rotating about a horizontal axis, the blast of abrasive being directed on to them. The abrasive falls through the perforations and is sifted through a dust separator and returned for re-use. Barrel plants are among the cheapest to operate, and are extensively used. They are, however, not suitable for very fragile parts; these are sometimes dealt with by putting small lengths of rubber hose into the barrel to prevent impact of the pieces on one another.

Another type of plant makes use of rotating tables on to which the parts to be cleaned are placed within the cabinet. This method

is especially suitable for flat parts, while for long components reciprocating tables are sometimes used.

Air Supply.—The air consumption of a blasting plant of this kind is considerable, the pressure used varying from 20 to 80 lb. per sq. in. Higher pressures give better rates of cleaning, but there is a corresponding increase in the rate of wear and tear of the plant, abrasive, and nozzles. Fig. 8 shows the air requirements for different diameters of nozzles under varying conditions of air pressure. The

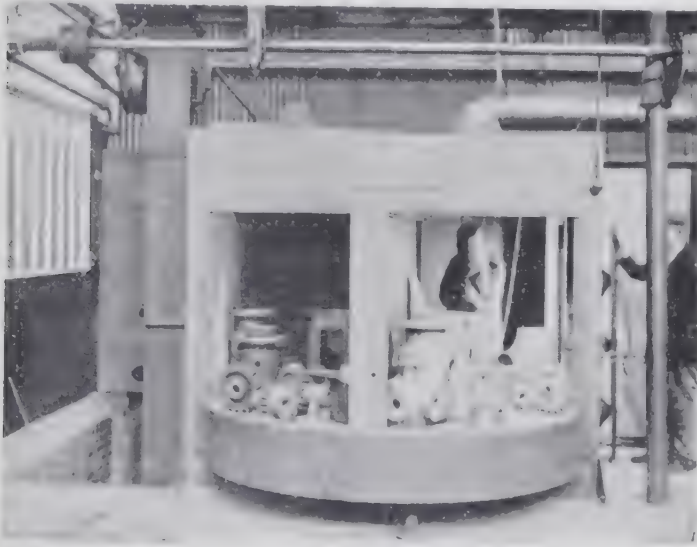


Fig. 6.—Shot-blast room in operation

Courtesy of Tilghman's Patent Sand Blast Co. Ltd.

nozzles are generally from $\frac{1}{4}$ in. to $\frac{3}{4}$ in. in diameter and are made of either cast iron, alloy steel, or special wear-resisting materials, such as sintered tungsten carbide or boron carbide. The rate of wear of the iron or steel nozzles is very high indeed, and as the bore increases, the air pressure must be correspondingly raised if the same velocity is to be imparted to the abrasive. For this reason, it is worth while using carbide nozzles, despite their higher initial cost, on account of the increased efficiency attainable with them. The life of such nozzles may be of the order of 1,500 hours, which is many times longer than that of the much cheaper cast-iron nozzles.

Centrifugal Blast-cleaning Plant.—A more recently developed type of plant has eliminated the need for compressed air. The abrasive is allowed to fall on to a rotating wheel or series of impeller blades from which it is projected centrifugally at high speed on to

the parts being cleaned. By careful design it is possible to control the direction of the abrasive grit very accurately, and better coverage can be obtained than by the use of nozzles and compressed air. The elimination of the air system simplifies the plant considerably, and it is claimed that the power consumption is lower, owing to the fact that much of the energy expended on the compression of the air in the pressure type of plant is lost and is not conveyed to the abrasive.

The centrifugal abrasive cleaning plant can be readily conveyerised, the parts being passed through the chamber continuously on a

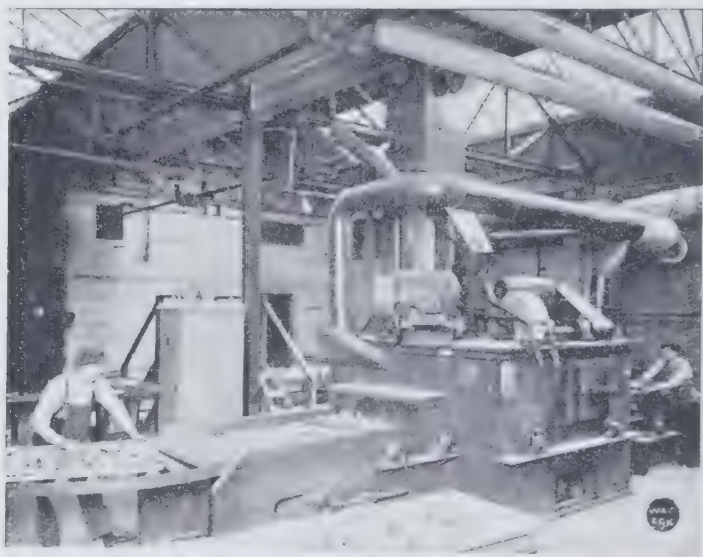


Fig. 7.—Conveyerised airless abrasive cleaner

[Courtesy of Tilghman's Patent Sand Blast Co. Ltd.]

moving belt. To minimise wear of the belt and the plant it is essential to keep the conveyor fully loaded with work, otherwise maintenance costs may become unduly high. The chief source of trouble in centrifugal cleaners is wear of the impeller blades; under unfavourable conditions these may require fairly frequent replacement. A hard alloy should be used for these blades, and it has been found that high-silicon iron withstands the abrading action particularly well. Fig. 7 shows a belt-conveyor type Wheelabrator airless abrasive cleaning plant engaged on the treatment of gas-cooker parts. The lay-out is particularly suitable for flat components. Generally speaking, this type of equipment presents many advantages, and the operating costs are often lower than when compressed air is employed, especially for smaller articles.

Abrasives.—Sand was at one time the chief abrasive used, but

it has, to a considerable extent, been replaced by such other materials as steel grit or shot. Sand is cheap and plentiful, but has the disadvantage that the dust generated as a result of its use constitutes a serious health hazard. This applies to many other natural abrasives which are used. Where sand is employed, it must be of the hard, coarse ocean variety, with a substantial quartz content for the optimum results. The size of the particles and their resistance to

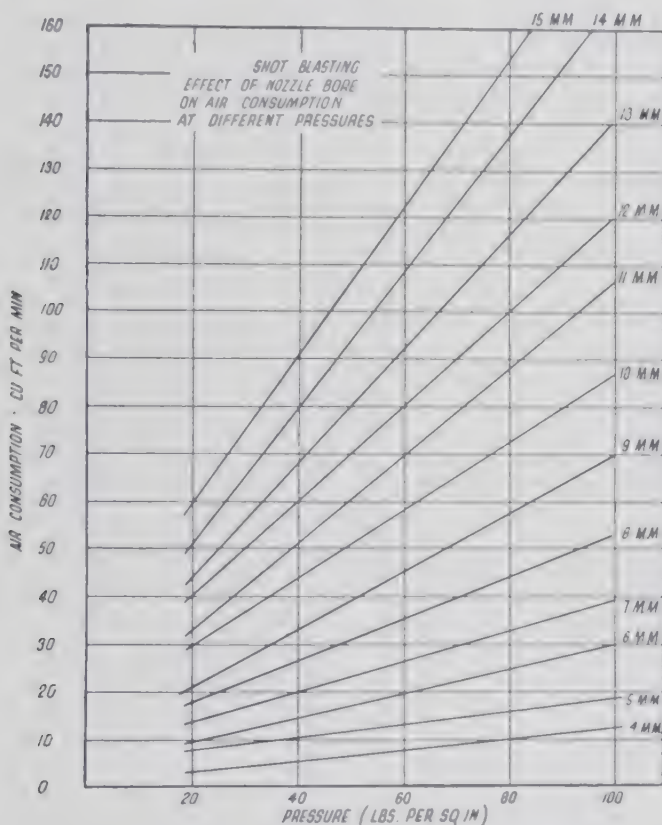


Fig. 8.—Effect of nozzle bore on air consumption

disintegration are important, and even with high-grade sand at moderate pressures it is to be expected that some 15 to 20 per cent will be disintegrated during each passage through the machine. The finer grades of sand are used for the cleaning of softer metals, such as brass and bronze, and also for sheet, while coarse sands are used for rough castings, etc. Sand is hygroscopic, and should be dried to remove water prior to use.

Steel Shot and Grit.—There has been an increasing tendency in recent years to use hardened steel shot, or grit, in place of siliceous

abrasives; grit is produced by crushing the round shot. Shot has a peening effect on the metal and does not give as nice a finish as do the finer grades of steel grit. The finer grits have, however, a shorter life than the coarser grades. All grit must be stored under dry conditions, as any rusting is liable to cause clogging of the machine and will reduce the cleaning efficiency of the grit itself.

The hardness of steel grit makes it especially suited for the descaling of steel castings covered with ingrained scale containing silica; the abrasive rapidly disintegrates if an attempt is made to sand-blast these. Steel grit in some cases gives a surface not quite so light in colour as sand-blasted metal, but this is not a serious disadvantage.

Despite the relatively high initial cost of steel abrasives, the advantages to be gained by their use are considerable. They may briefly be summarised as follows: (1) reduced dust formation and elimination of risk of silicosis in operators; (2) much longer life of abrasive; (3) greater uniformity of abrasive, and hence more uniform cleaning; (4) less frequent cleaning of equipment and sieving of the abrasive; (5) higher efficiency for a given power consumption.

Stainless Steel.—The descaling of stainless steel by blast methods demands the use of stainless steel shot, alumina or iron-free sand. Iron-containing materials becoming embedded in the steel surface markedly reduce the corrosion-resistance of stainless steels. The shot must also be kept free from fine particles or fragmentary material of foreign origin if the best results are to be obtained.

Maintenance of Plant.—Blasting equipment needs careful maintenance if the best results are to be obtained. Thus, small leaks in abrasive hose connections result in loss of power and efficiency. Similar considerations apply to worn nozzles, which should be replaced in good time. Static charges sometimes build up on rubber hose, which are liable to give the operator an electric shock, and may result in perforation of the hosing. The use of conducting rubber (loaded with graphite) eliminates this source of trouble.

Water in the compressed air is undesirable, and steps should be taken to eliminate it either by a good after-cooler on the compressor or by means of a suitable water-trap. A most efficient centrifugal automatic air dehumidifier is now available which can be directly installed in the pipe-line.

The centrifugal type of plant demands careful attention to the balance of the impeller blades. If one blade wears prematurely, the whole set-up is thrown out of balance, so that severe vibration and

damage to the machine and bearings may result. Special abrasive cleaning equipment is a desirable adjunct to every type of plant, as an abrasive containing a high proportion of dust will give poor results. Proper ventilation is also needed to prevent abrasive accumulating in undesired parts of the machine and making for poor working conditions. Good maintenance also eliminates delays due to blockages in the pipe system.

Light scales can also be removed by barrel-tumbling, but the hard nature of the scale makes the process a slow one, and may result in its being driven into the metal surfaces.

Vapour Blasting.—A recent development is the vapour blast or abrasive sludge cleaning process. In this method the abrasive medium, usually synthetic alumina of suitable grain size is suspended as a sludge in water and fed by gravity to a nozzle where it is projected on to the articles being cleaned, by means of a steam or air blast. This results in a very fine and smooth type of cleaning action which leaves the metal in a clean, matt condition, very suitable for subsequent polishing and plating operations, etc. Where steam is used the heat of the process leaves the work substantially dry, but with compressed air rapid rusting will occur unless the work is oiled immediately after treatment. A corrosion inhibitor is also often added to the abrasive sludge.

THE PICKLING OF FERROUS METALS

By far the greatest amount of descaling by pickling is carried out on iron and steel, and the process constitutes a major industrial operation. Thus, all steel sheet must be pickled before tinning or galvanising, and in Great Britain about $1\frac{1}{2}$ million tons of steel are pickled annually in the course of these processes alone. For this reason, the pickling of ferrous metals merits special attention.

Composition of Scale.—The scale formed on steel under conditions of oxidation in air at high temperatures has been very thoroughly investigated, and the subject has been reviewed by Pfeil and Winterbottom.⁽¹⁾

In the case of metals, such as iron, copper, lead, and aluminium, the volume of the oxide produced is greater than that of the original metal, so that the scale will tend to protect the latter from further oxidation under conditions of high temperature. Broadly speaking, the rate of scaling follows a parabolic law: $W^2 = Kt$ where W is the weight of oxide formed and t is the time, K being a constant. In actual practice, however, cracking of the oxide takes place so that as the film thickens, it tends to peel off and the rate of oxidation is

increased. High temperatures and rapid rates of heating promote cracking and flaking of the oxide film, although this may occur even at relatively low temperatures. Rapid fluctuations of temperature are conducive to the cracking of oxide coatings.

Heat-resisting alloys, such as the nickel-chromium alloys and the high-chromium steels, owe their properties to the formation of an impervious oxide film, which is not subject to flaking and adheres so tightly that oxygen diffusion is prevented.

It is generally considered that the oxide formed when iron is heated is made up of three distinct layers:

- (a) The outermost layer, which is relatively thin and contains the highest proportion of oxygen and consists of ferric oxide, Fe_2O_3 .
- (b) An intermediate layer, which is rather thicker and consists of magnetic oxide of iron, Fe_3O_4 .
- (c) A relatively thick layer in proximity to the iron, containing the highest proportion of the latter element and having a composition approximating to the formula FeO . This layer probably does not actually consist of the compound FeO , but is a solid solution termed "wüstite," which decomposes below 570°C . into a eutectoid of iron and magnetite, Fe_3O_4 . In the case of scale formed below this transition temperature the innermost layer of scale contains Fe_2O_3 or Fe_3O_4 , or a mixture of both.

The precise composition and the structure of the scale may be modified in practice, as has already been mentioned, by the conditions under which heating is carried out. Fig. 9 shows the rate of scale formation at various temperatures in an air current flowing over a heated iron surface at the rate of 1 cm. per second.

In the case of rolled steel, the actual rolling temperature plays an important part in the amount of scale formed. Thus higher temperatures cause the formation of heavier scales, which, moreover, contain a higher proportion of ferrous oxide. Eisenkolb⁽²⁾ found that when rolling was carried out in a temperature range of 650°C . to 800°C ., the scale consisted of 63.7 per cent FeO and 36.3 per cent Fe_2O_3 . On the other hand, with rolling temperatures of 500°C . to 600°C . the FeO content fell to 49.9 per cent, with 49.1 per cent Fe_2O_3 . This has a profound effect on pickling, as will be seen below.

Acids used.—Scale removal from ferrous metals is carried out by

pickling in a solution of sulphuric or hydrochloric acid. When castings are concerned, silicates and sand are often mixed with the scale, and hydrofluoric acid is necessary to dissolve away the siliceous material. Welding scale is also apt to contain fused silica or iron silicates, due to the electrode coatings. Hydrofluoric-sulphuric acid mixtures at temperatures of 160° F. to 170° F. are useful in this case. Acids other

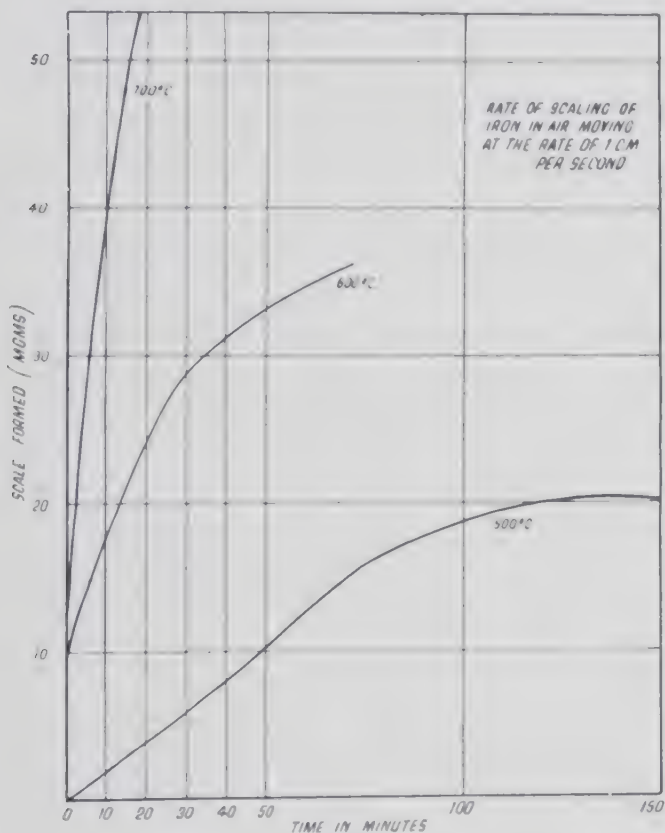
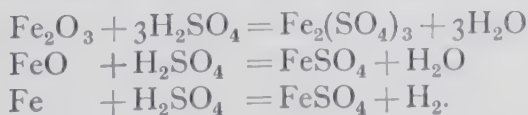


Fig. 9.—Rate of scaling of iron in air moving at 1 cm. per second

than these are not usually employed. The removal of the scale occurs as a result of: (a) the chemical dissolution of the scale coating; and (b) a “splitting off” of the scale as a result of the gas liberated during the action of the acid on the basis metal.

With sulphuric acid, the reactions which take place are largely confined to the two lower oxides and the metallic iron, viz.:



Reduction of the ferric sulphate occurs through the presence of nascent hydrogen:



The corresponding reactions with hydrochloric acid are:



Reduction of ferric chloride by nascent hydrogen:



The dissolution of magnetite, Fe_3O_4 , in either acid is slow, this oxide being soluble in acids only with great difficulty.

The solubilities of iron, FeO and Fe_2O_3 , in these acids have been determined by Bablik⁽³⁾ (Table VI).

It will be seen that in the case of the lower concentrations of hydrochloric acid a substantial proportion of the total attack takes place on the iron base; with acid of 10 per cent concentration, however, considerable dissolution of the oxides occurs. In highly concentrated hydrochloric acid the pickling reaction is more in the nature of a chemical dissolution of the scale than mechanical removal.

TABLE VI
SOLUBILITIES OF IRON AND ITS OXIDES IN PICKLING ACIDS

Temp. C.	Acid concentration per cent	Dissolved from 100 gm. sample in 1 hour		
		Fe (gm.)	Fe_2O_3 (gm.)	FeO (gm.)
20°	H_2SO_4 :	6.0	3.9	0.14
20°		15.0	4.8	0.56
20°		35.0	6.4	0.98
40°		97.7	9.0	1.4
20°	HCl:	20.8	0.112	0.48
20°		31.6	0.36	0.76
20°		40.7	0.71	0.83
20°		50.1	1.6	1.8
20°		72.0	10.6	7.5

With sulphuric acid at lower concentrations the weight of oxide dissolved as compared with that of metallic iron is considerably greater than is the case with hydrochloric acid at corresponding concentrations. The dissolution of the oxide in sulphuric acid at all concentrations plays a very important part in the pickling reactions.

In the case of sulphuric acid at all concentrations the ratio of metallic iron dissolved to that of the oxides is much greater at elevated temperatures than at room temperature.

The ferrous oxide (FeO) layer in contact with the steel is the most soluble of the oxides present in scale; hence, where a substantial amount of this oxide is present in actual proximity to the steel surface, more rapid pickling will take place than when the higher oxides are located there. During pickling the acid penetrates to the FeO layer through pores and fissures in the scale, so that the dissolution of the FeO in the acid results in the splitting off of the surface layers of scale. This accounts for the difficulty in removing scales formed at temperatures below 570° C., as has already been mentioned. Thus, Pilling and Bedsworth⁽⁴⁾ found that when annealing is carried out for one hour at 500° C. to 550° C., the iron particles in the "wüstite" phase agglomerate and the growth of these particles makes pickling difficult even with strong acids.

Bablik⁽⁵⁾ has shown that in pickling with sulphuric acid, the proportion of the scale which is removed by being split off, as opposed to that removed by being chemically dissolved, is greater in the case of sulphuric acid than with hydrochloric acid. This is a factor which makes for greater economy in acid consumption when the former acid is used. The contact between the scale and the metal also plays an active part in the pickling process, as a potential difference exists between the metal and the oxide, with the result that

TABLE VII
EFFECT OF TEMPERATURE ON PICKLING TIME

Acid	Pickling time in mins.		
	18° C.	40° C.	60° C.
5 per cent H ₂ SO ₄ . .	135	45	13
10 per cent H ₂ SO ₄ . .	120	32	8
5 per cent HCl . .	55	15	5
10 per cent HCl . .	18	6	2

the electro-chemical cells formed in the presence of the acid are able to facilitate its dissolving action.

In the case of sulphuric acid, raising the temperature is more effective in increasing the rate of dissolution of metal and oxide than with hydrochloric acid. Metallic iron is also much more soluble in the latter acid than is the scale, and this difference is greater than is the case with sulphuric acid.

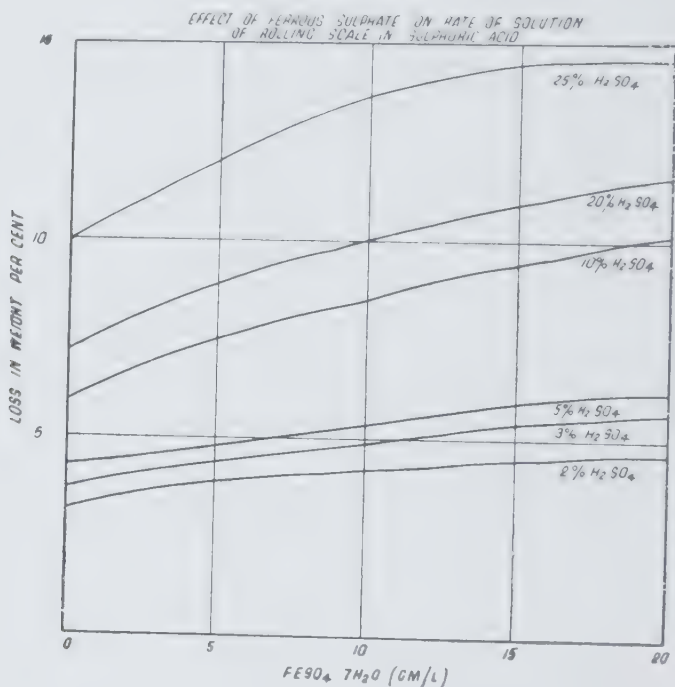


Fig. 10.

Sulphuric Acid.—The best commercial sulphuric acid has a concentration of about 95 per cent; its action on iron and steel is small. Starting from a dilute acid solution, it is found that, as the concentration of the acid increases, the pickling time decreases until it reaches an optimum at about 25 per cent strength; the pickling rate then falls rapidly. On the other hand, the effect of temperature is very marked. Thus Bablik⁽⁶⁾ in some tests on the pickling of scaled steel shown in Table VII found that increasing the temperature of 5 per cent sulphuric acid from 18° C. to 60° C. reduced the pickling time to about one-tenth. For this reason, sulphuric acid pickling should be carried out in the hot acid for maximum efficiency.

As iron sulphate builds up in the solution, however, the rate of pickling is reduced. Fig. 10 shows the speed of pickling of rolling

scale in the presence of ferrous sulphate.⁽⁷⁾ The scale contained 47.3 per cent FeO and 51 per cent Fe_2O_3 . The restraining effect of ferrous iron salts in pickling solutions is less at elevated than at low temperatures, both in sulphuric and in hydrochloric acids, due to the greater solubility of the salts at higher temperatures. At low concentrations of sulphuric acid the effect is less marked than with

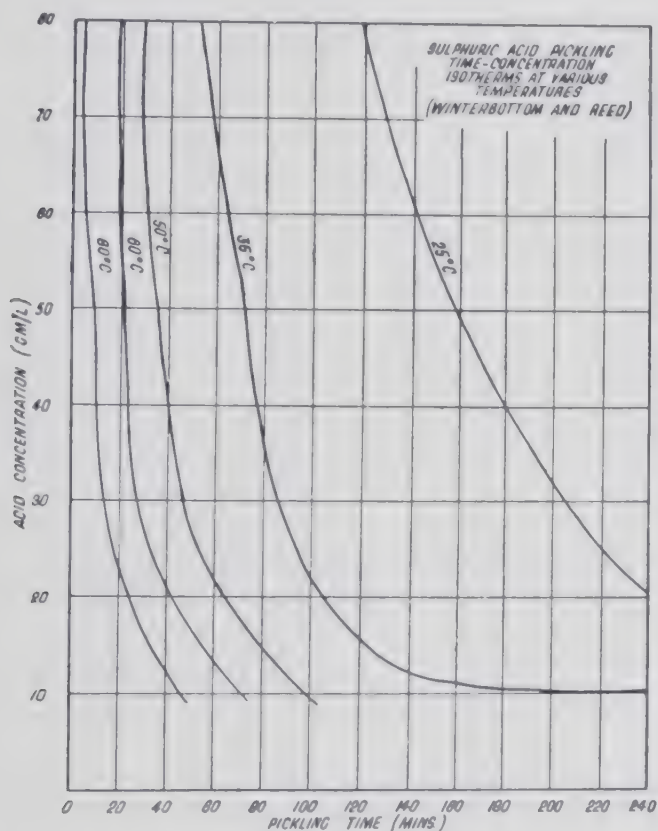


Fig. 11.—Sulphuric acid pickling: Time-concentration isotherms

higher concentrations. Ferric salts accelerate the rate of pickling, but this is only of academic interest, since the trivalent iron content of a pickling solution is normally negligible.

Although in the case of hydrochloric acid the presence of iron can speed up the rate of pickling within certain ranges of temperature and acid concentration, excessive concentrations of iron salts in all acid solutions reduce the rate of pickling very considerably. Winterbottom and Reed⁽⁸⁾ quote 80 gm. per litre of iron as the maximum that can be tolerated in sulphuric acid pickling baths, whilst in hydrochloric acid baths the maximum practical limit is given as 120 gm. iron per litre.

Hydrochloric Acid.—Commercial hydrochloric acid consists of a solution in water of 30 to 35 per cent of hydrochloric acid gas. The volatility of the acid makes its use impracticable at elevated temperatures; above 40° C. the rate of loss of acid is very rapid indeed. In actual practice the pickling speed is increased by higher concentrations of acid rather than by elevated temperatures. In this

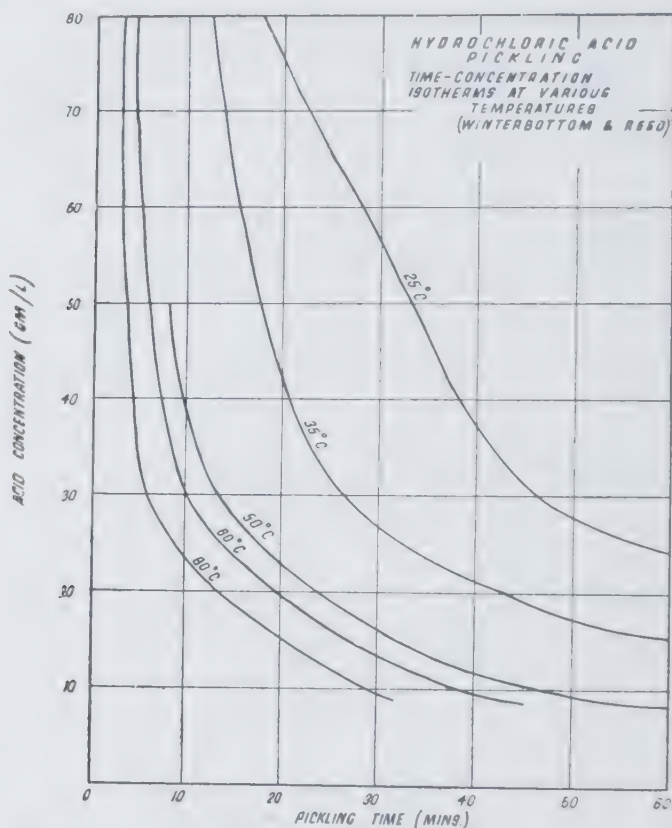


Fig. 12.—Hydrochloric acid pickling: Time-concentration isotherms

respect, hydrochloric acid differs from sulphuric acid; in the latter case concentration is of little influence, the chief method of increasing pickling rates being by elevating the temperature (cf. Figs. 11 and 12). The relative non-volatility of sulphuric acid and its lower cost makes it the more generally employed pickling acid.

The addition of hydrochloric acid to sulphuric acid is sometimes practised. Pickling is accelerated by such additions and the higher solubility of ferrous chloride enables the solution to be used rather longer before it is discarded.

One type of mixed acid pickling process developed by de Lattre

and used to some extent on the Continent, has been described by McLeod.⁽⁹⁾ It makes use of a solution containing 1 gm. mol. of ferrous sulphate, 1 gm. to 2 gm. hydrochloric acid, and 1 gm. mol. of sulphuric acid per litre, at a temperature of 50° C. to 56° C.; gelatine is added as an inhibitor. It is claimed that the entire pickling is carried out by the sulphuric acid, the hydrochloric acid simply serving to regenerate the sulphuric acid according to the equation:



the equilibrium being shifted to the right. When a concentration of about 350 gm. per litre of ferrous sulphate is reached, the latter is crystallised out by cooling, the crystals centrifugally separated and iron oxide and sulphuric acid recovered by a roasting process. (See p. 67.)

Sludge Formation.—After pickling, a layer of adherent black sludge remains on the metal surface; much of this sludge also accumulates on the bottom of the tank. In sulphuric acid pickling, the deposit contains up to 0.6 per cent of the iron dissolved in the acid; with hydrochloric acid the amount of sludge produced is substantially less. This sludge also contains a high proportion of the nobler metals present in traces in the steel being pickled, and these are precipitated on to the steel surface. An analysis of sludge deposited on steel sheet showed the presence of up to 20 per cent copper, 7 per cent nickel, and 6 per cent arsenic; the steel had only a content of 0.18 per cent copper, 0.08 per cent nickel, and 0.43 per cent arsenic.

The use of hydrochloric acid thus tends to give a smoother and whiter pickled surface than does sulphuric acid, and is therefore favoured in some tinning operations despite its higher cost and slower action.

The thorough washing of pickled metal to remove these deposits is important and will be referred to again. (See p. 50.)

Inhibitors.—In the pickling of ferrous metals the scale is very often partially lifted in some areas before the general surface has been descaled. Various materials have, therefore, been developed for addition to pickling baths to reduce attack on the basis metal without appreciably affecting the rate of descaling. Such materials are also valuable, inasmuch as their presence lessens hydrogen evolution (and hence the likelihood of hydrogen embrittlement), and the formation of pickling blisters on sheet metals due to the pressure of occluded hydrogen below the metal surface.⁽¹⁰⁾ (See p. 54.) They also reduce roughening and pitting due to excessive metal dissolution. This excess

acid consumption and loss of weight of metal can be considerable. Thus, it was found that in pickling 1,000 sq. ft. of steel sheet (both sides) for fifteen minutes in a bath containing 3.5 per cent of sulphuric acid at 200 °F. without an inhibitor, 6 lb. of scale were removed accompanied by a loss of 65 lb. of metal. Over 90 per cent of the acid was used in dissolving excess iron over and above that required for the descaling process proper.

It has long been known that arsenic and antimony precipitated on a steel surface will materially reduce the rate of attack of the latter by acids; these elements cannot, however, be used in practice as inhibitors. Gelatine, glue, and resinous materials have been used as inhibitors, their action depending on their colloidal nature; more recent research, however, has indicated the types of compounds most likely to be useful as inhibitors.

The modern commercial inhibitors are extremely effective. In some recent tests carried out by Hoare and Hedges⁽¹¹⁾ on commercial inhibitors, the high effectiveness of these materials was shown by the fact that whereas steel sheet dissolved at the rate of 2,474 mgm. per hour in 8 per cent sulphuric acid, the addition of 0.05 per cent of various inhibitors reduced the rate of dissolution to 35 to 112 mgm. per hour. In hydrochloric acid, at 20 °C. the results were less striking, the reduction being from 35 mgm. per hour to 10 mgm. per hour by the addition of 0.05 per cent of inhibitor in the best example given.

An inhibitor should be completely stable in the pickling acid even at elevated temperatures, be easily and completely soluble in the acid, and retain its efficiency on prolonged storage. In other words, the first essential in an inhibitor apart from its efficacy in this direction, is that it should be a highly stable compound. It must also not be prone to form films on the metal surface which will be difficult to remove and so interfere with subsequent processing, such as galvanising, enamelling, or electro-plating, and, of course, it should effectively reduce attack by the acid on the bare metal surface, and minimise hydrogen evolution.

The pickling inhibitors of commerce are available as foaming and non-foaming types. The purpose of the former is to produce a blanket on the surface of the solution so as to prevent the liberation of unpleasant acid spray. Unfortunately, excessive foam formation may cause the inhibitor to concentrate in the surface layer, which is undesirable. Inhibitors are only added in very small quantity, e.g. of the order of 0.05 to 0.10 per cent of the pickling acid. They are sometimes mixed with diluents to aid in stabilising them or to increase

their solubility. In any case, there is a definite optimum concentration above which their effectiveness does not increase.

Pickling inhibitors are nowadays usually well-defined chemical compounds of high molecular weight. The inhibiting action appears to depend on the presence of certain chemical groupings. The types of compounds in general use are organic derivatives containing

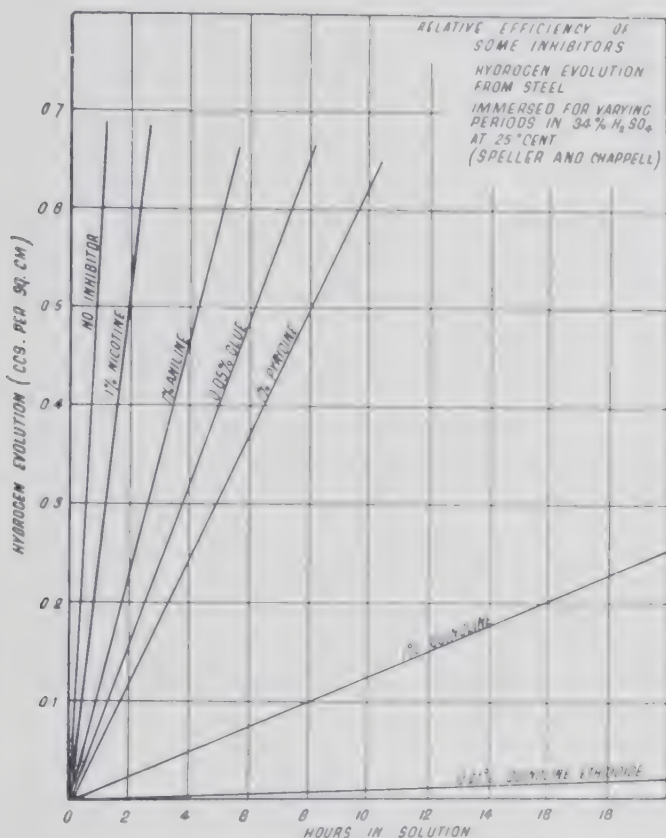


Fig. 13.—Relative efficiencies of inhibitors

nitrogen, oxygen, sulphur, or other elements of the fifth and sixth Periodic Groups. Heterocyclic nitrogen compounds (such as pyridine and quinoline) are especially effective. Other substances, such as substituted ureas and thioureas, mercaptans, aldehydes, ketones, and organic acids find application. The properties of the inhibitor are determined by the length and characteristics of the hydrocarbon and polar portions of the molecules and their stereo-chemical arrangement.⁽¹²⁾

The relative efficiencies of some compounds as inhibitors are shown graphically in Fig. 13.

Theory of Inhibitors.—The mechanism by which inhibitors act has been the subject of much controversy. It is held in some quarters that adsorption probably occurs so that attack by the acid on the metal is inhibited. An alternative explanation has been advanced⁽¹³⁾ to the effect that the additive increases the hydrogen over-voltage. Hydrogen evolution is considered to take place preferentially at local inclusions in the metal surface and at grain boundaries which behave cathodically. The discharge of cations at these zones inhibits the evolution of hydrogen and hence reduces the attack on the metal.

Stainless Steels.—The pickling of stainless steels bears no relation to the technique used with other ferrous metals, because the nature of the scale on these metals is essentially different.

The austenitic stainless steels, containing 18 per cent nickel and 8 per cent chromium, are commonly pickled in nitric-hydrochloric or nitric-hydrofluoric acid mixtures. One typical solution consists of equal volumes of water and commercial hydrochloric acid, containing about 5 per cent of nitric acid, used at 50° C. to 60° C.; another solution contains 6 per cent nitric acid and 0.6 per cent hydrofluoric acid, used at similar temperatures.

An alternative process makes use of two successive baths into which the metal is immersed:

Solution I

Sulphuric acid	.	.	.	.	15 per cent
Hydrochloric acid	.	.	.	.	5 per cent
Water	.	.	.	.	Balance

Temperature, 60° C.

Solution II

Nitric acid	.	.	.	.	20 per cent
Hydrofluoric acid	.	.	.	.	0.5 per cent
Water	.	.	.	.	Balance

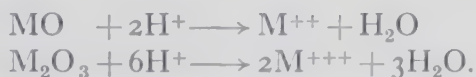
Temperature, 30° C. to 40° C.

The metal should be rinsed between the two pickles. Inhibitors are desirable in these pickling acids, but they generally lack stability when in the presence of nitric acid, so that they are decomposed in solution relatively quickly. It will be observed that these solutions consist of an acid, together with an oxidising agent (i.e. nitric acid). The purpose of the latter is to oxidise the lower oxides of the metals present in the alloys to the comparatively soluble higher

oxides, which are then more readily dissolved by the acids present. The use of other oxidising agents has been introduced in place of nitric acid, which results in the liberation of dangerous fumes of oxides of nitrogen, and is generally unpleasant. Dichromates have been employed more particularly in sulphuric acid pickling baths for non-ferrous alloys, such as brass, but one of the important developments of recent years in pickling practice has been the increasing use of ferric sulphate. The material was first introduced as a pickling agent in 1935, and by 1940 50,000 tons of metal per annum were being pickled in the U.S.A. in ferric sulphate-containing solutions.⁽¹⁴⁾ In this country the use of this material in pickling is much less advanced.

Ferric Sulphate Pickling.—Ferric sulphate is available as a product consisting of the anhydrous salt $\text{Fe}_2(\text{SO}_4)_3$, in the form of a dry granular powder. It has long been known that the presence of ferric sulphate in a sulphuric acid pickling solution greatly increases the rate of attack on steel and results in etching of the metal surface. It is therefore undesirable in ordinary pickling solutions, although under normal conditions of pickling of steel, oxidation of the ferrous sulphate to the ferric state is unlikely to occur.

In the electro-chemical series, the ferric ion (Fe^{+++}) is preceded by zinc, chromium, iron (ferrous), nickel, hydrogen (H^+), and copper. Typical generalised pickling equations for ferric sulphate solution would be, for descaling:



In the presence of an acid, a combined oxidation and descaling action may occur corresponding to the equation:



where M is a metal usually before ferric iron in the series.

In making up a ferric sulphate pickling solution for stainless steel, this material replaces the nitric acid; a concentration of three to six parts of ferric sulphate to one part of hydrofluoric acid is used. The best results are obtained when the composition of the bath corresponds to the theoretical formation of ferric fluoride in the solution, according to the equation:



The solution is then colourless and practically fumeless, owing to the fact that little free hydrofluoric acid is present. Excessively high

hydrofluoric acid concentrations cause too much attack on the steel, whilst if the ferric sulphate concentration is too low the rate of pickling will be much reduced.

The ferric ion probably holds the fluoride in a complex by a buffering action, so that the actual concentration of fluoride ion is maintained at a sufficiently high level to enable descaling to take place, but in insufficient concentration for attack on the steel to occur.

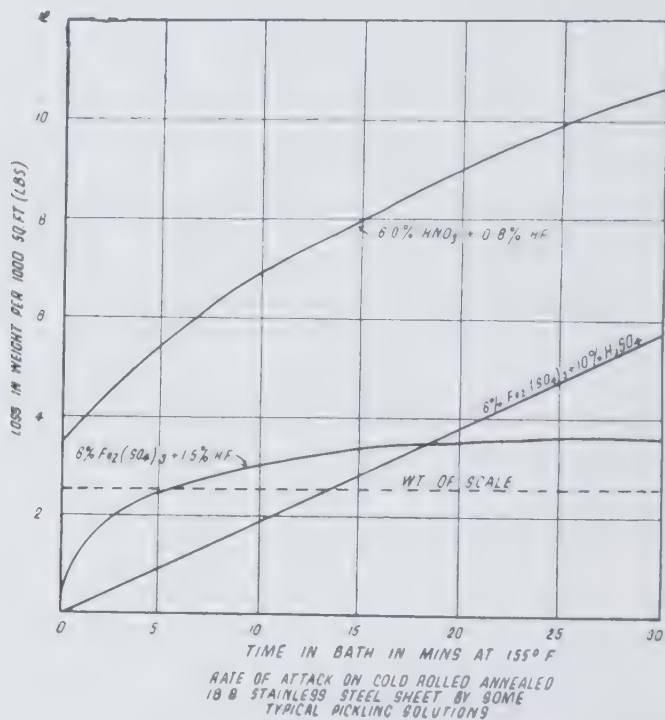


Fig. 14.

A solution employed by the author with complete success in removing particularly difficult scale from austenitic stainless steel sheet contained 12 per cent of ferric sulphate and 3 per cent of hydrofluoric acid, the bath temperature being 150° F. to 260° F. The pickling time required was an average of ten to fifteen minutes. The advantages presented by this method of pickling are as follows: (i) the pickling operation is practically free from fumes and spray when the solution is in balance; (ii) the attack by the solution on stainless steel is negligible at those areas where the scale has been removed, due to the passivating effect of the ferric sulphate on the metal.⁽¹⁵⁾ This is very important in view of the difficulty of obtaining an inhibitor which will be stable in pickling solutions of the conventional type.

These latter pickles attack the descaled stainless steel surface relatively quickly as soon as it is exposed to the action of the acids (see Fig. 14).

When scales have been formed in a strongly reducing atmosphere it may be desirable to increase the ferric sulphate concentration beyond the proportions already mentioned, as such scales will contain more lower oxides and will therefore require the presence of a relatively higher concentration of oxidising agent. On the other hand, scales formed in highly oxidising atmospheres will require a greater relative proportion of hydrofluoric acid. Increasing the overall concentration of the pickling solution and the temperature increases the rate of pickling.

The high chromium irons do not pickle so satisfactorily in this type of solution as do the austenitic stainless steels, and present many difficulties under practical conditions. Ostrofsky⁽¹⁶⁾ has, however, described a process for pickling high chromium iron involving an electrolytic treatment at 25 amps. per sq. ft. in fused caustic soda, which may help in overcoming some of the difficulties. The use of ferric sulphate in the pickling of non-ferrous metals has also been introduced in recent years. (See p. 72.)

Sodium Hydride Process.—An important development in descaling technique has been the introduction of the sodium hydride method in recent years for dealing with difficult scales. In this process the articles are immersed in a bath of fused caustic soda containing 1.5–2.5 per cent of sodium hydride. The hydride is generated within the bath by the interaction of sodium and cracked ammonia. The generator consists of a welded mild steel box open at the bottom with a hole at the top large enough to admit blocks of sodium, and covered by a lid. This box is immersed in the caustic soda for a depth of 12–15 in., projecting about 6–8 in. above it. The cracked ammonia is introduced into the box through steel tubes which are carried about 9 in. below the liquid level. The gas then bubbles through the molten caustic soda, and meets the layer of molten sodium floating on the surface inside the generator.

The bath is without effect on the basis metal, and acts by reducing the oxides present on the metal to a finely divided metal powder or a flaky foil. Chromium oxide is not fully reduced, but is converted to a loosely adherent lower oxide. Once the metal reaches the temperature of the bath, descaling takes place very rapidly; the operating temperature is 350°C. to 370°C. The same bath will deal with almost all types of scale.

Treatment of small parts is carried out in baskets, whilst larger

parts are suspended by hooks. They should be dry and preferably pre-heated before immersion in the bath. After treatment the parts are allowed to drain for a minute or two and quenched in cold water. This causes steam to be liberated which washes away the reduced scale, after which they can be spray rinsed and washed in hot water to remove residual caustic soda.

For stainless steel a bright dip in 10 per cent nitric acid with about 1 to 2 per cent of hydrofluoric acid is recommended.

The plant required consists essentially of a heated arc-welded mild steel tank; the temperature of the bath is thermostatically controlled. Great care must be exercised in taking articles out of and immersing them in the bath owing to the corrosive nature of the caustic alkali. **Protective clothing and goggles are essential.**

Wetting Agents in Pickling.—The application of wetting agents and surface active materials to pickling practice is a relatively new innovation, and certainly their use appears to present advantages. There are a variety of materials which are able to bring about a very considerable reduction in the surface tension of aqueous solutions when they are added to the latter in very small amount. Typical examples of compounds of this kind are the alkyl naphthalene sulphonates, the quaternary ammonium compounds with long hydrocarbon side-chains, and the aliphatic sulphonates (e.g. sulphosuccinic acid esters). Very many of these wetting agents are available under commercial names; their constitution and field of applications have recently been the subject of an excellent review by Snell.⁽¹⁷⁾

Wetting agents for pickling must be stable in the acid and should not result in excessive foaming. By lowering the surface tension of the pickling acid, better penetration of the scale by the acid is obtained and hydrogen bubbles are more readily liberated, thus enabling the acid to reach the metal surface more rapidly and uniformly. Moreover, the tendency for sludges to adhere is reduced. Finally, less acid is lost by drag-out, so that a reduction in total acid consumption is effected.

Hartshorn⁽¹⁸⁾ describes instances where the use of a wetting agent in a pickling solution has enabled slightly greasy material to be satisfactorily pickled without the need for a preliminary degreasing operation.

Washing after Pickling.—Thorough washing after pickling is essential, as considerable amounts of acid-containing iron salts adhere to the metal when it is lifted from the pickling solution, as has already been stated. If imperfectly washed off, these salts set up

corrosion, and can contaminate subsequent processing tanks (galvanising baths, plating solutions, etc.) into which they may enter. Residual salts can also accumulate in pores in the metal and can subsequently ooze out, damaging any finishing coat that may have been applied. Thus, in one case the author found that rapid corrosion of the nickel-plated brass holders of electric-light bulbs occurred after only a few hours' service. The corrosion products contained a very large proportion of nitrates, which resulted from the retention of nitric acid or nitrates in the pores of the brass during pickling, and these found their way through the nickel-plate when the lamp-holders became heated whilst working.

Pickled metal should first be washed in running cold water, preferably using high-pressure spray-jets. It should then be washed in another running water tank, this second tank being kept practically uncontaminated with incoming acid residues. The metal is then immersed again in very hot water to dissolve residual salts, being left in the tank for a sufficiently long time to acquire the temperature of the water. This will effect the removal of most of the acid from the metal pores. Sufficient heat will also be retained for the metal to dry off spontaneously unless it is of very thin section.

On removal from the water, pickled steel is liable to rust very quickly; this tendency is usually reduced by the addition of lime to the final hot-water rinse. Even better temporary protection can be obtained by the addition of about 1 per cent of phosphoric acid to the water, which results in the formation of a thin phosphate film on the steel surface.

Phosphoric acid can be used alone as a pickling acid for steel; in this case it is employed at a concentration of approximately 15 per cent and at a temperature of about 160 F., but the relatively high cost of the acid is against its general use. It has the advantage that any traces of acid which may be left behind will not, in general, promote corrosion, in view of the insolubility and non-hygroscopic nature of the heavy metal phosphates.

ELECTROLYTIC PICKLING

In electrolytic pickling the metal is made either the anode or the cathode in an acid solution or in a solution of a neutral salt. Anodic pickling is to be preferred since hydrogen is not liberated at the anode so that hydrogen embrittlement does not occur, as it may do when cathodic pickling is employed. The scale is chiefly removed as a result of the mechanical effect of the gas liberated by electrolysis at the metal surface. Dilute sulphuric acid is often used as the

electrolyte, current densities of 20 to 100 amps. per sq. ft. being employed. The difficulties of applying the current and uncertainty as to whether the results are worth the relatively elaborate equipment needed have limited the general application of the process.

The Bullard-Dunn Process.—The Bullard-Dunn method of electrolytic pickling has, however, had some measure of success, and a number of plants have been installed for dealing with difficult pickling propositions. The process is described by Kronsbein.⁽¹⁹⁾

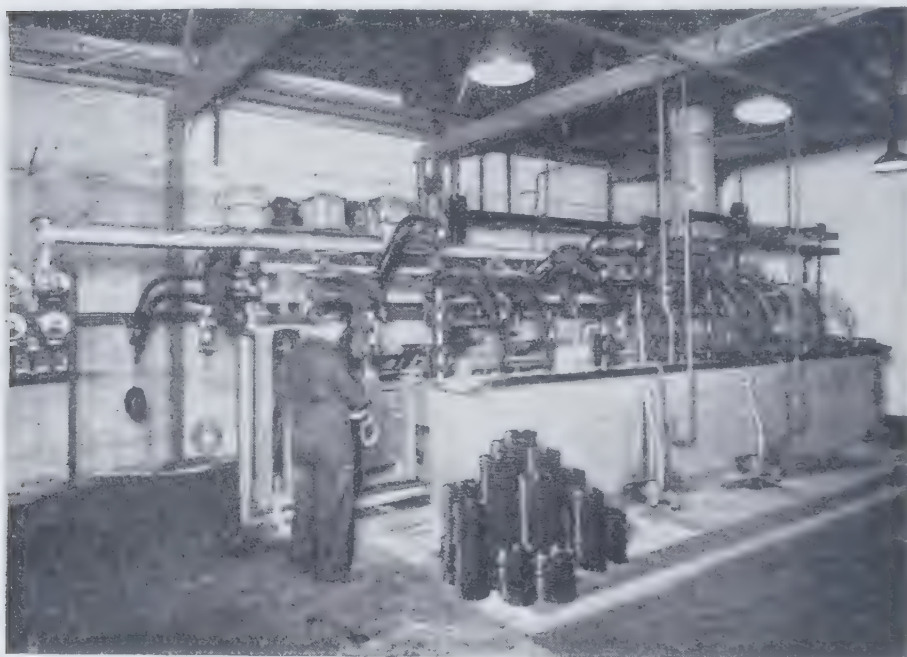


Fig. 15.—Bullard-Dunn pickling plant

[Courtesy of W. Canning & Co. Ltd.]

The electrolyte consists of a hot dilute sulphuric acid pickle of the normal type containing about 0.1 per cent of tin sulphate. The current density employed is high—of the order of 60 to 80 amps. per sq. ft., the articles to be descaled being made the cathodes. The anodes are of high-silicon iron, a small percentage of them being of tin in order to maintain the tin content of the solution.

As pickling proceeds, immediately an area becomes descaled, metallic tin is deposited on to it, and this inhibits further attack by the acid on that area; when all the scale has been removed, the surface is left covered with a thin film of tin. The theory of the process is that a counter e.m.f. is generated on the cleaned surface equal to the hydrogen over-voltage of the tin; simultaneously, the

current density on the areas where the scale remains is raised, due to the rise in voltage which occurs across the electrolytic cell through the reduction in current density at the descaled surfaces. Thus, local accelerated pickling takes place as the descaled areas become larger. The tin does not build up beyond a very thin layer, subsequent thicknesses being spongy and non-adherent in nature.

Metal descaled by this process is subject to hydrogen embrittlement, but this can be relieved. (See p. 56.) The tin deposit may be left on the surface, forming a good undercoat for subsequent painting or enamelling; alternatively, it can be removed rapidly by anodic treatment in caustic soda. Silicon-iron cathodes are used on to which the tin is deposited, and these can then be put into the pickling bath, so that the tin is recovered.

Corrosion tests in salt water on rolled steel window-frame sections, descaled by the Bullard-Dunn process and painted, showed that the amount of corrosion produced was only 50 per cent of that obtained by painting directly on to shot-blasted and phosphate-coated material. When samples from which the tin had been removed were exposed, the performance of these finishes was about equal.

Fig. 15 shows a view of a roundabout type of automatic plant for the pickling of steel parts by the Bullard-Dunn tin process.

Electrolytic pickling should not be confused with electrolytic polishing or brightening as applied to stainless steel and other metals. This will be described in the section on polishing methods.

HYDROGEN EMBRITTLEMENT

When hydrogen is liberated at a steel surface from a solution either during pickling, electro-plating, or electro-alkaline cleaning, a proportion of the hydrogen is adsorbed by the metal surface and diffuses into the interior of the steel. Such hydrogen is liberated in the atomic state, and it is in this form that it is absorbed; molecular hydrogen does not diffuse into iron or steel at the temperatures prevailing in these operations. The mechanism whereby the hydrogen diffuses into the steel is thought to depend on absorption of the relatively small hydrogen atoms within the iron lattice.

The hydrogen present is not uniformly distributed throughout the metal, but is concentrated chiefly near the surface. The absorption of hydrogen also appears to be catalysed by the presence of elements such as phosphorus, sulphur, and arsenic, which are capable of forming hydrides.⁽²⁰⁾

The quantity of hydrogen absorbed may be quite considerable, and has two major effects in relation to metal finishing: (a) while it

is present in the steel an embrittlement of the metal takes place; (b) on subjecting the metal to high temperature finishing processes, especially galvanising or enamelling, the gas is liberated with the formation of blisters in the steel surface or within the protective coating.

Edwards⁽²¹⁾ investigated the rate of diffusion of hydrogen through mild steel sheet of different thicknesses, and found that the amount

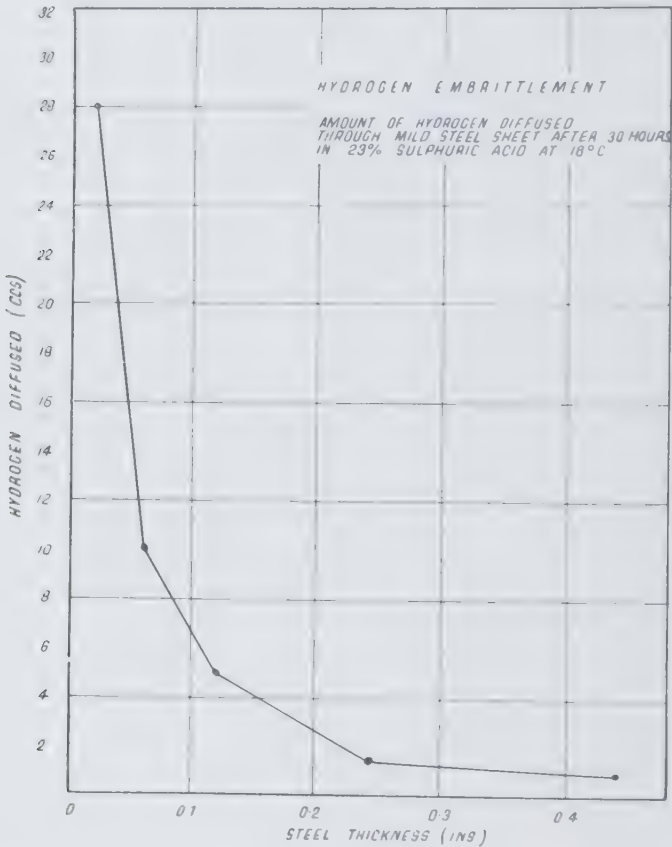


Fig. 16.

of hydrogen diffusing at room temperature was roughly inversely proportional to its thickness (Fig. 16). As the temperature rises the amount of hydrogen diffused decreases appreciably, although it must be borne in mind that under practical conditions of acid pickling there is simultaneously an increase in the total hydrogen liberated as the temperature of pickling increases. Broadly speaking, those factors which are conducive to an increased rate of attack by the acid on the metal, e.g. higher temperature, greater acid concentration, or the use of more active acids, all lead to a reduction in the ratio of the amount of hydrogen diffusing through the metal to the

total hydrogen liberated. Thus Zapffe and Sims⁽²²⁾ found that increasing the acid pickling temperature from 20° C. to 80° C. increased the hydrogen absorption thirtyfold, but the ratio of liberated to absorbed hydrogen was found to have increased fivefold. On balance, probably, the shorter pickling period resulting from the use of higher pickling temperatures causes a net reduction in the amount of hydrogen absorbed in a given time.

Recent work by Zapffe and Haslem⁽²³⁾ on hydrogen embrittlement resulting from the copper plating of steel indicates that the cathode efficiency of the plating process has little bearing on the amount of hydrogen absorbed or the degree of embrittlement produced. Thus some processes developing no visible cathodic gassing whatsoever produced the greatest embrittlement, considerably exceeding the effect of straight "hydrogen plating", i.e. cathodic pickling. In this respect copper plating is similar to cadmium, zinc and chromium plating processes. It is interesting to note that processes which do not produce adherent coatings also do not produce embrittlement, and reagents added to baths to change the characteristics of the plate also change the characteristics of embrittlement, so that each condition requires separate evaluation.

Effects of Embrittlement.—The effects of hydrogen absorption manifest themselves in an embrittlement of the steel, although it is important to distinguish between loss in mechanical strength due to roughening of the metal surface in pickling and that caused by hydrogen absorption. Sutton⁽²⁴⁾ determined the bending angles to which steel could be subjected before fracture as a measurement of the degree of hydrogen embrittlement. Noble⁽²⁵⁾ has investigated the crushing strength of tubular-shaped test-pieces which had been treated by the Bullard-Dunn electrolytic pickling process. The pieces were broken by transverse loading between parallels on a tensile testing machine, and it was found that the breaking load of test-pieces cleaned by pickling was only some 35 per cent of those cleaned by sand-blasting. In view of the fact that the Bullard-Dunn process does not appreciably roughen the surface of the metal, practically the whole effect can be ascribed to hydrogen absorption. Noble found that susceptibility to hydrogen embrittlement in general increases with hardness. The maximum susceptibility occurs at the temper brittle range of 500° F. to 550° F., except in steels that are not subject to a temper brittle range, e.g. molybdenum-bearing steels, in which case the temperature of maximum susceptibility is much lower. The presence of a hardening constituent, e.g. carbon, increases susceptibility to embrittlement as does decreasing section.

more important factor in the elimination of embrittlement than is the duration of heating. Stainless steel is particularly susceptible to embrittlement.

Of the plating processes, it is of interest to note that it was found that chromium produces the greatest amount of embrittlement and lead the least, while for plates of equal thickness, tin was the easiest to relieve and silver the most difficult. Embrittlement could be removed by heating in water, air, or oil, or by ageing at room temperature, the effectiveness of the respective media being in this order. (Other authorities find that relief takes place more rapidly in water or oil than in air at the same temperature.⁽²⁷⁾) Complete restoration of the crushing strength of the test-pieces was obtained by heating for one hour at 290 F., or half an hour at 400 F. in air.

Table VIII shows the results given by various treatments tested for the relief of hydrogen embrittlement caused by pickling (Bullard-Dunn process).

PICKLING PLANTS AND THEIR OPERATION

Acid pickling was, until comparatively recent years, regarded as a very crude process not amenable to close control. Fumes and poor working conditions were considered inseparably associated with pickling operations. To-day, however, it is possible to operate a pickling plant under conditions as good as those prevailing in many other parts of a factory.

Towards achieving this, the manufacturers of pickling equipment have contributed in no small measure. Early plant for pickling consisted of tanks made of wood, such as pitch pine, bolted together and strengthened with metal reinforcement. Pickling tanks have also been made of slate, stone, or even of concrete, covered with bituminous or asphaltic coatings. These proved successful to a varying degree, but there was always the difficulty of leaking joints. Available acid-resisting jointing compositions are seldom capable of withstanding the expansions and contractions of tanks of this description and of resisting acid penetration, especially when hot sulphuric acid is used. Wood tanks are lined with chemical lead when sulphuric acid is the pickling medium to ensure their non-permeability to acid; lead-lined tanks are, however, not suitable for hydrochloric acid, although they can be used with hydrofluoric acid pickles. The interior of the tank is usually covered with boarding over the lead to prevent mechanical damage to the soft metal lining. Steel tanks are lead-lined similarly, but, whereas perforation of the lead lining of a wood tank leads to little serious damage to the tank proper

and can be readily repaired when leakage of acid becomes evident, a steel tank may be very seriously injured by acid-leakage through the lining. Fig. 17 shows a pickling plant consisting of six lead-lined wood vats. Two tanks are used for pickling, there being two cold rinse vats, one neutraliser, and one hot-water dip tank. A framework carries bearings and guide-blocks for drums containing the parts to be pickled.

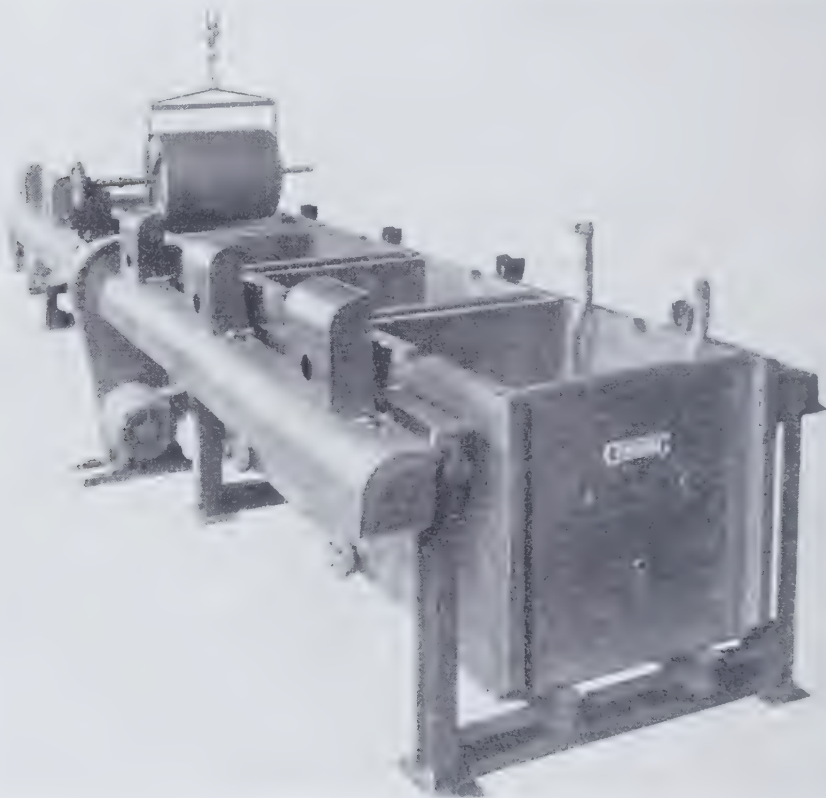


Fig. 17.—Lead-lined timber pickling plant

Courtesy of W. Canning & Co. Ltd.

The newer types of pickling tanks are often constructed of acid-resisting brick, which is impervious to the liquor, combined with special cements between the bricks. Such bricks and compositions are also used for the pickling shop floors and for the drainage installations.

A further development consists in the use of non-metallic pickling tanks, constructed of laminated synthetic resin-impregnated fibrous materials of various kinds, the resins being usually of the phenol-formaldehyde thermosetting type. These are quite unaffected by

pickling acids (except highly oxidising acids), and will withstand the temperatures used in pickling processes. The materials are also successfully used in the manufacture of pickling baskets and racks for carrying parts to be pickled.

The application of a proprietary material of this type to pickling processes has been described by Reavell;⁽²⁸⁾ it will withstand temperatures up to 130°C. without softening, and is not affected by hydrochloric, phosphoric, and sulphuric acids (the latter in concentrations up to 50 per cent). It is also resistant to most organic acids and solvents. Oxidising acids such as nitric acid will attack the material, but it is claimed that in the presence of hydrochloric acid in the concentrations employed in mixed acid pickling such attack is inhibited. Thus a mixture of hydrochloric acid (40 parts) and nitric acid (10 parts) can be safely used in such equipment. It is, however, unsuitable for handling caustic alkalis. These synthetic resin-based substances can be machined, joined, or, best of all, autogenously moulded into storage tanks, glandless acid pumps, fan-blades and units, immersion heater casings, and many other components where their advantages are manifest.

Rubber.—Perhaps the most important development in pickling plant has been the introduction of rubber and ebonite tank linings. These are usually applied to steel, being homogeneously bonded to the metal; such bonds are of great strength and tenacity. Various cements are employed, such as sulphonated rubber derivatives made by milling sulphuric acid into rubber. A thermoplastic cement for bonding rubber to metal may also be produced by heating rubber with sulphuryl chloride for several hours at 125°C. to 130°C. Other methods have been summarised by Messenger.⁽²⁹⁾ It is also possible to bond soft rubber linings to wood and even to concrete, although the harder rubber linings are to be preferred, being more resistant to acids and high temperatures.

In the best types of rubber-lined steel pickling tanks a soft rubber lining is cemented to the tank to take up any stresses that may develop in service, and this is followed by an inner lining of hard rubber, the whole being then vulcanised. The commoner practice is, however, to use a single hard rubber layer on the steel. Sometimes the outside of the tank is rubberised to prevent external corrosion, but this is a refinement. More usually protection for the outside of the plant is obtained by means of bitumen paints.

An acid-resisting brick lining over the rubber serves to prevent the latter from mechanical damage. Such tanks are capable of giving many years of trouble-free service. The linings are applicable to

hydrochloric acid pickling, and to solutions containing hydrofluoric acid at temperatures up to 150 F. Plants of these types are shown in the accompanying illustrations. Fig. 18 illustrates a reinforced concrete tank lined with rubber and protected by blue-bricks in acid-resisting cement. Figs. 19 and 20 show two bar-pickling installations of similar construction.

Another important development has been the use of suitable plastics (e.g. Vinylite, a vinyl co-polymer) in sheet form for tank



Fig. 18.—Rubber and brick-lined concrete pickling tank

[Courtesy of Nordac Ltd.]

linings in place of rubber. These plastics have the advantage over rubber of being unaffected by oxidising acids under most conditions of ordinary use.

Armour-plate glass tanks for pickling have also recently been introduced in the U.S.A.

Exhaust System.—It is essential to have a really effective exhaust to withdraw fumes from the tanks. The old overhead hood type of exhaust is antiquated, obstructive, and inefficient. Modern plants use cross-ventilation through a narrow duct running along the length of the tank on one side, or, if the tank is wide, on both sides. The ducting may be made of lead-lined timber, rubber-lined steel, etc. Asbestos composition ducts have been used, but have the

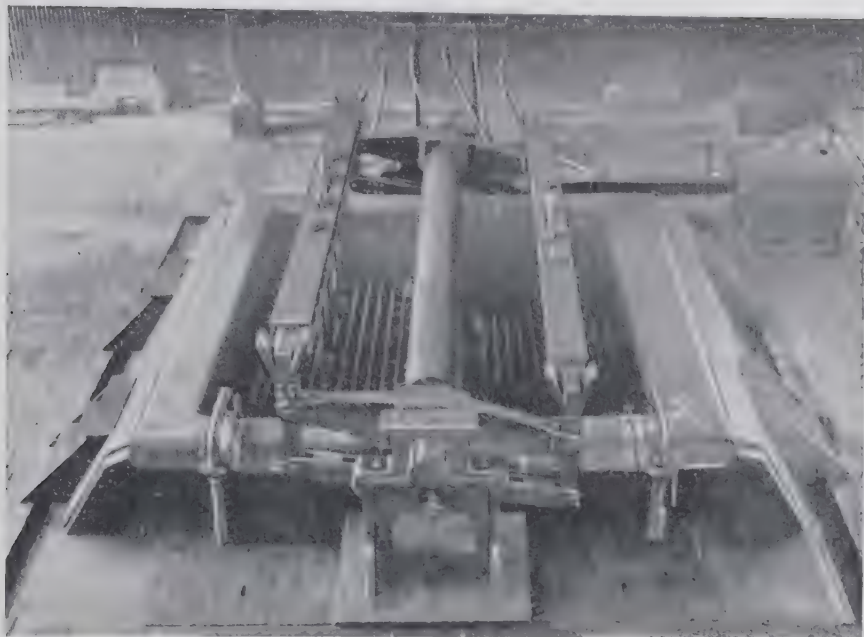


Fig. 19.—Bar pickling plant

[Courtesy of Nordac Ltd.]

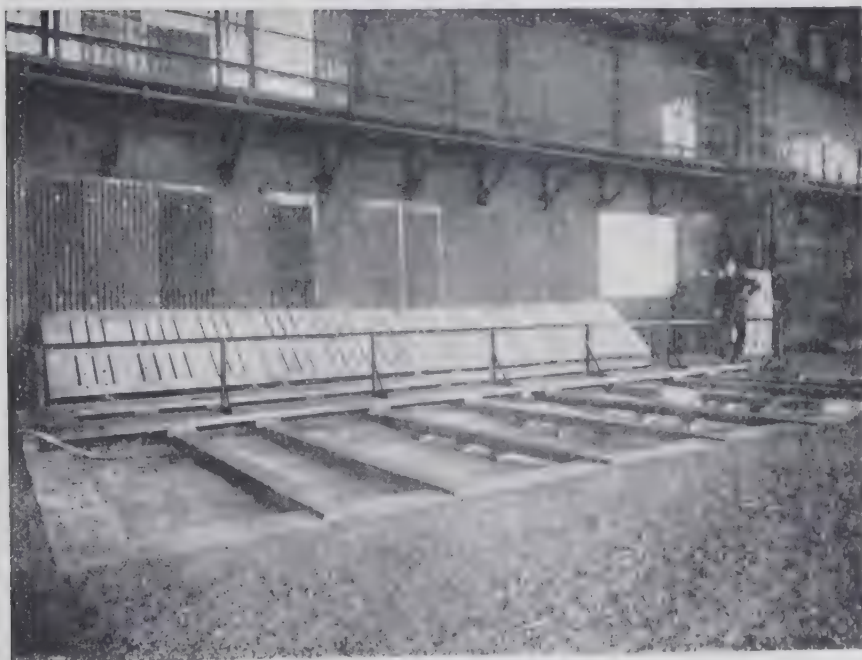


Fig. 20.—Bar pickling plant

[Courtesy of Nordac Ltd.]

disadvantage of being brittle. The fans should be of adequate power and the blades can be made of laminated resin material, or of steel, protected by an acid-resisting coating, which may be of the resin-type or of rubber. Fume ducting is best made from rubber-lined steel; this type of construction gives great flexibility of design and facilitates the installation of a fume exhaust system which can be relied upon to give trouble-free service for a very long time.



Fig. 21.—Conveyorised pickling plant

[Courtesy of W. Canning & Co. Ltd.]

Pickling Baskets.—Pickling baskets are necessary for the handling of large quantities of parts and were at one time made of resinous wood. Again, their life was short, and nowadays acid-resisting metals are in successful use. Of these metals, perhaps one of the most generally applicable is Monel metal, which is essentially a 70 : 30 nickel-copper alloy. High chromium stainless steels are important because of their acid resistance, whilst nickel-chromium alloys withstand hydrochloric acid well, although their cost is high. Fig. 21 shows such pickling baskets in use on a steam-heated plant fitted with an overhead conveyor for transferring the work from the pickling to the rinsing, neutralising, and hot-water drying tanks.

An interesting material for pickling accessory plant is high-silicon

iron, containing up to about 14 per cent of silicon. This resists hot dilute acids satisfactorily, but has the disadvantage that it cannot be machined. Fabrication must therefore be carried out by casting and grinding.

Heating.—The heating of pickling tanks is commonly carried out by means of live steam injected through a pipe into the solution. The impingement of the steam on the bottom of the tank is, however, undesirable and is to be avoided, if possible. To this end, several types of rotating and stationary injectors have been developed for attachment to steam pipes to enable the steam to be introduced more uniformly into the solution. The fact that the introduction of considerable quantities of vapour may tend to dilute the solution unduly makes it desirable to use coils if possible; these can be constructed of lead-covered steel. Electric heaters have been successfully used and can be made of a suitable metal or alloy or of fused silica.

Ebonite-covered steel steam coils have been installed, despite their relatively low heat-transfer qualities. One type of ebonite covering $\frac{1}{16}$ in. thick is, however, said to possess a heat transfer coefficient of more than 15 B.Th.U. per sq. ft. per hour per degree Fahrenheit difference in temperature.

Gas-heated pickling plants are also used. Direct heating below the tank by open flames is not satisfactory, but gas burners can be injected from the side of the tank into pipes running through the latter near the bottom and connected to a vertical flue-pipe. A particularly interesting method of gas-heating is the Kemp system, where the gas-air mixtures are correctly proportioned by a special carburettor and burned inside a tubular flue system consisting of a recirculating rectangle. Located at the side of a pickling tank the unit not only gives cheap and efficient heating, but also enables the liquid to be kept in circulation by the convection currents produced.

Heating coils should be raised above the level of the tank bottom, to prevent them being covered by sludge, which will greatly reduce the rate of heating. Similar considerations apply to agitators for pickling solutions; these should not be located directly on the bottom of the tank or sludge will tend to be stirred up.

Hoists for the transfer of crates of components to be pickled are available, the motors being of special enclosed construction to enable them to function in the presence of steam and acid fumes.

Agitation of the Solution.—It is desirable to have some form of agitation of the pickling bath, since this aids in removing the hydrogen from the metal surface and enables fresh acid to reach the metal continuously. Agitation can be obtained in hot solutions by

the steam injector; when coils are used, a certain amount of movement of the solution is obtained by convection currents.

Cold hydrochloric acid solutions in particular are apt to stratify unless some form of agitation is introduced, and even in hot solutions agitation is desirable. One of the reasons for the better action in practice of hot sulphuric acid pickles, as compared with low temperature hydrochloric acid, is probably connected with the good circulation of the acid obtained as a result of heating.

Movement of the solution can be obtained by a suitable mechanical method for rocking or oscillating pickling baskets in a vertical direction, by the use of electrically driven screws or paddles in the solution or by compressed air. The first method is the most commonly practised, but most small plants operate without the use of such devices. Some interesting types of automatic pickling plant for small parts using travelling and rotating barrels have been developed in recent years, and their use has greatly reduced pickling times.

Cleaning.—The pickling acids do not readily remove grease, and the presence of even a thin film of oil anywhere on the surface of the metal will reduce the rate of pickling over the area concerned tremendously. In sheet mills, where pickling is carried out soon after heat treatment, no preliminary degreasing is generally necessary, but in engineering works, where the likelihood of oily contamination of the metal surface is considerable, it is essential to degrease the metal before pickling. This can be satisfactorily carried out in hot alkaline cleaners, with or without the application of current, or, better, by degreasing in trichlorethylene vapour (Chapter IV). The latter process is, however, a more costly one. The use of wetting agents in the pickling acid can help in some instances in the pickling of slightly greasy work. One development worthy of mention is the pickling of metals in pressure spray plants constructed of acid-resisting materials.⁽³⁰⁾ Brass shell-cases have been successfully pickled in this way in 10 per cent sulphuric acid to remove oxide scale after annealing. It is claimed that the method enables the pickling time to be very considerably shortened, whilst the mechanical action of the spray results in the more effective removal of loosely adhering scale and sludge. Steel pickled in this way also shows relatively little hydrogen embrittlement. A considerable number of such plants have been installed and have given good service.

Process Control.—Sulphuric acid baths are made from the strong acid, purchased preferably as the purer and more concentrated commercial grade, having a density of 1.84 (66 Bé.), and containing

95 to 97 per cent sulphuric acid. Good-quality acid is desirable as the presence of contaminants, such as arsenic in any quantity, will materially reduce the rate of pickling, as has already been pointed out.

Hydrochloric acid is purchased in the form of a 30 to 35 per cent solution. A 10 per cent solution of the commercial acid can, therefore, be made up approximately by adding one part of the acid to two parts of water by volume. The pickling solutions commonly employed vary from 5 to 10 per cent in acid content, and once a suitable concentration has been decided upon, daily acid additions must be made to maintain the strength.

✕ **Analytical Control.**—The acid concentration can be determined by direct titration of the solution with standard caustic soda, using phenolphthalein as an indicator. A practical innovation suitable for use on the plant consists in adding pellets of sodium bicarbonate containing a little phenolphthalein to a sample of the pickle taken in a suitable measure. Each pellet can be of such a weight as will correspond with the presence of 1 per cent of acid in the pickle. The number of pellets which have to be added to the sample before the solution turns pink is then a measure of the percentage of the acid present.

The iron content should also be determined at frequent intervals, since the accumulation of iron salts in the acid reduces the rate of pickling. After a time it is not feasible to add more acid, and the solution must be discarded and a new one made up. Density measurements alone do not give a true indication of the acid and iron contents of the bath, since both these constituents simultaneously influence the density of the solution.

Winterbottom and Reed⁽³¹⁾ have constructed nomograms which are useful and are adequate for control purposes relating the iron and acid contents and the density of the pickling solution in degrees Twaddle for both sulphuric and hydrochloric acid pickling. For sulphuric acid the nomogram has been based on the relation: $[Fe] = 2.0(T - 0.132[H_2SO_4])$, and for hydrochloric acid, on $[Fe] = 2.56(T - 0.098[HCl])$. Analytical methods are, however, generally applicable and easy to carry out. As all the iron in the solution is in the ferrous state titration with standard potassium permanganate solution enables the iron content to be directly determined. In the case of hydrochloric acid solutions it is necessary to add manganous sulphate and phosphoric acid to prevent oxidation of the acid to chlorine, and to prevent the development of the ferric iron coloration.

Colorimetric papers for the rapid determination of iron in pickling

solutions can be prepared by dipping filter paper strips into a 1 per cent solution of ammonium thiocyanate in acetone. By treating these with a series of standard solutions of ferric chloride, red colours corresponding to each concentration of iron can be obtained; these colours can then be compared with the colour produced by a drop of the pickling solution which is to be tested. The iron in the pickle should have been oxidised previously to the ferric condition by the addition of a few drops of nitric acid.

As has already been stated, when the iron content reaches 8 per cent in the case of sulphuric acid and 12 per cent in hydrochloric acid, the pickling rate is reduced to such an extent that the bath must be discarded. In actual practice it is often not an economic proposition to run sulphuric acid pickling baths with an iron concentration in excess of 6 per cent, or hydrochloric acid baths containing more than 9 per cent of iron.

The operating temperature in sulphuric acid pickling is best kept at about 140°F. in the case of new solutions, gradually raising the temperature as the iron content builds up, to 160°F. to 165°F. The pickling operation itself may take from three to twenty minutes, depending on the thickness and condition of the scale. Excessively long pickling times are to be avoided in order to prevent subsequent processing difficulties, and if successful scale removal is not effected in a relatively short time, changes should be made in the pickling process itself (by altering the acid, temperature, etc.), rather than by attempting to obtain the required results by extending the duration of pickling.

Pickling Wastes.—The waste acid must be neutralised in suitable units by means of alkali before being run into the drains. The time-honoured method is to pass the waste acid through a chamber built of acid-resisting brick and containing lime, often mixed with steel swarf to prevent consolidation of the neutraliser. Mulcahy⁽³²⁾ recommends the use of a lime slurry for neutralising pickling wastes, mixing the slurry with the acid at the point where it enters the neutralising pit, and agitating the mixture by means of air or a pump. The best arrangement consists of a two-compartment tank; the smaller compartment is the mixing chamber where both milk of lime and waste acid are fed together in appropriate proportions. The mixed lime and acid solution then passes over a weir into the larger compartment where the sludge is kept in suspension by means of perforated air pipes at the bottom. When neutralisation is complete the tank contents are discharged into the sewers by means of a pump or a steam ejector. (See Fig. 84, p. 261.)

For the neutralising plant the best method of construction is to use an outer wall of reinforced concrete, asphalt or rubber, lined with an inner protective lining of Staffordshire blue brickwork set in siliceous or resinous cement. The weir walls must be liquid-tight and built and lined integrally with the outer walls to ensure this.

The ferrous salts can be recovered by crystallisation from spent sulphuric acid pickling solutions in specially designed plants, and this system is being increasingly adopted where large-scale pickling operations are carried out. The waste acid liquor containing iron equivalent to 85 per cent of maximum solubility is pumped into a crystalliser filled with coils through which refrigerated or deep well water is circulated. The crystalliser is also fitted with a jacket through which the water circulates, and the acid is meanwhile rapidly stirred. By lowering the temperature of 10 per cent sulphuric acid to 20° C. from 60° C. the iron content of the solution can be reduced to about 6 per cent in about 2 hours.

The ferrous sulphate crystals formed in cooling are precipitated at the bottom of the crystalliser (which is conical in shape) when the stirrer is stopped. The regenerated acid is pumped back for further pickling, the crystals being run off, drained, washed and dried in a centrifuge.

Acid recovery plants of this type are extremely economical in use, and enable the pickling process to be carried out under close control and at relatively low temperatures. The ferrous sulphate crystals find industrial applications.

Pickling acid wastes are also oxidised and ferric sulphate obtained from them. This commodity is now available commercially as a dry, granular, non-hygroscopic salt and finds many useful applications. One of its uses is in the pickling of stainless steel and non-ferrous metals. (See pp. 47 and 72.)

Ferrous sulphate also undergoes thermal decomposition and useful products can be obtained from it by heating the material in retorts. On heating in air at fairly low temperatures the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ crystals lose 3 molecules of water of crystallisation until the lower hydrate $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ is reached. At 167° C. this compound is oxidised to basic ferric sulphate; this in turn decomposes at 492° C. (in practice, temperatures of 550° C. to 600° C. or more may be used) into iron oxide, Fe_2O_3 , and sulphur trioxide, SO_3 , which is readily converted into sulphuric acid by absorption in water, or better, in fairly strong sulphuric acid. The iron oxide finds useful application as a paint pigment and in the manufacture of polishing rouge.

Three patented methods of decomposing ferrous sulphate in practice are worthy of mention. In the first, the ferrous sulphate is

mixed with about 30 per cent of its weight of iron oxide, Fe_2O_3 , and 1 per cent of sodium carbonate to neutralise free acid; it is then dried and sintered at 750°C . to 850°C ., when sulphur trioxide is evolved, leaving Fe_2O_3 .⁽³³⁾ A similar process is described by Clarkson.⁽³⁴⁾ In a more recent method the iron sulphate is roasted and treated with ammonia gas and water to produce ammonium sulphate and iron oxide.⁽³⁵⁾

PICKLING OF NON-FERROUS METALS

The chief non-ferrous metals which present any real descaling problems in industrial practice are the copper alloys (including brasses and bronzes) and the heat-resisting alloys of the nickel-chromium and the nickel-chromium-iron types. Light alloys are pickled in acids if necessary, and the presence of hydrofluoric acid will usually remove any silica which may be present in the case of castings.

Copper Alloys.—The oxide film formed on copper when the metal is heated to a high temperature in air consists of an outer scale of cupric oxide (CuO), under which is an inner scale of cuprous oxide (Cu_2O). The outer scale is in a state of stress and may flake off in cup-shaped fragments.

At lower temperatures, up to about 600°C ., the rate of oxidation is parabolic, approximately following the law:

$$\text{Rate of oxidation} = Ae^{-Q/RT},$$

where A and Q are constants, R the gas constant, and T is the absolute temperature.

Dunn⁽³⁶⁾ studied the oxidation of the brasses at different temperatures, and found that all alloys with less than 80 per cent of copper oxidise at practically the same rate over the range 580°C . to 880°C . The copper oxide produced at the metal surface is reduced by zinc diffusing from the interior, so that the scale consists of practically pure zinc oxide. With a copper content of 80 to 90 per cent in the alloy, the rate of zinc diffusion is unable to keep pace with the rate of copper oxide formation so that the scale becomes progressively richer in copper. With a 90 per cent copper—10 per cent zinc alloy, the oxide layer contains 90 per cent of copper.

The factors influencing the type of scale which will be formed on brass are therefore: (a) the rate of diffusion of oxygen through the oxide; (b) the degree of oxidation of the metal; (c) the diffusion of zinc to the metal surface; (d) the reduction of copper oxide by metallic zinc; and (e) the re-entry of copper into the metal surface. When the rate of diffusion of the zinc is not rapid enough, the

mechanism breaks down and normal oxidation takes place. Arsenic (up to 0.2 per cent) and nickel (up to 1 per cent) are without effect on the oxidation of brass, but aluminium strongly inhibits the rate of scaling; thus the presence of only 1.9 per cent of aluminium will lower the rate of oxidation to one-fortieth of its value in the absence of this element. The effect is probably due to the reduction of the zinc and copper oxides by the aluminium.



Fig. 22.—Pickling and recovery plant for copper rod

Courtesy of W. Canning & Co. Ltd.

Copper and its alloys are commonly pickled in 10 per cent hot sulphuric acid under similar conditions to those prevailing in the pickling of ferrous metals, although obviously ferrous and non-ferrous alloys must not be treated in the same bath. The oxide is removed largely by chemical dissolution; this type of pickling is mainly applied to the descaling of alloys in connection with deep-drawing or pressing operations. The process needs careful control as contamination of the solution by foreign metals, such as iron, may influence the rate of pickling; defects such as tarnishing or various types of discoloration may also manifest themselves.

Fig. 22 shows a plant for the pickling of copper rods combined with an acid recovery unit. The work travels through the tank (which contains 20,000 gallons of sulphuric acid) on an overhead runway.

Sulphuric acid pickling is applied to brass primarily as a descaling operation, after which the surface can be polished if required. The

appearance of the metal is rather dull and usually shows a good deal of local variation in colour.

Bright Dipping.—Where a bright surface is required, as is often the case, the brass is usually subsequently dipped in a solution of nitric and sulphuric acids, containing approximately 55 to 60 per cent by weight of sulphuric acid, and 8 to 10 per cent of nitric acid—the rest being water. Sometimes a small amount of sodium chloride or hydrochloric acid is added. The function of this constituent (which should not be present to the extent of more than 0.25 per cent) is to reduce the rate of attack on the copper and to increase it on the zinc so that a brighter finish results. The direct action of nitric acid alone on brass brightens the metal rapidly, but it is very violent and difficult to control. The use of a “dipping acid” similar to the above is therefore most generally practised, since it enables the operation to be more easily controlled, and, moreover, a longer life is obtained from the nitric acid (which is the more expensive constituent of the mixture). This is because the metallic nitrates which are first produced are converted to sulphates, thus setting free more nitric acid for active work.

It is preferable to use two dipping baths, the first containing spent acid, to which a little hydrochloric acid has been added. After immersion in this the metal is passed quickly through the second bath, the object being to avoid contaminating this latter solution as much as possible. The brass is then very well washed in several rinses of water and dried in hot sawdust. It is then ready for lacquering, plating, etc. Good ventilation is essential in nitric acid pickling, owing to the dangerous oxides of nitrogen which are liberated.

As considerable heat develops in the reaction the acid must be kept cool, usually by immersion of the stoneware vessel in which it is kept in an outer tank containing running cold water, as at temperatures above 35° C. the dipped surface tends to become dullish.

The addition of chromic acid to the bath has been recommended to reduce the reaction rate and to inhibit the evolution of nitrous oxide. The treated parts can then be handled more evenly, and drag-out losses are reduced whilst the brass is to some extent passivated. A typical composition of this type can be made up from:

Sulphuric acid	80 c.c.
Nitric acid	20 c.c.
Hydrochloric acid	1 c.c.
Chromic acid	55–60 gm.
Water	200 c.c.

This solution has been used on a fairly large scale in the U.S.A.

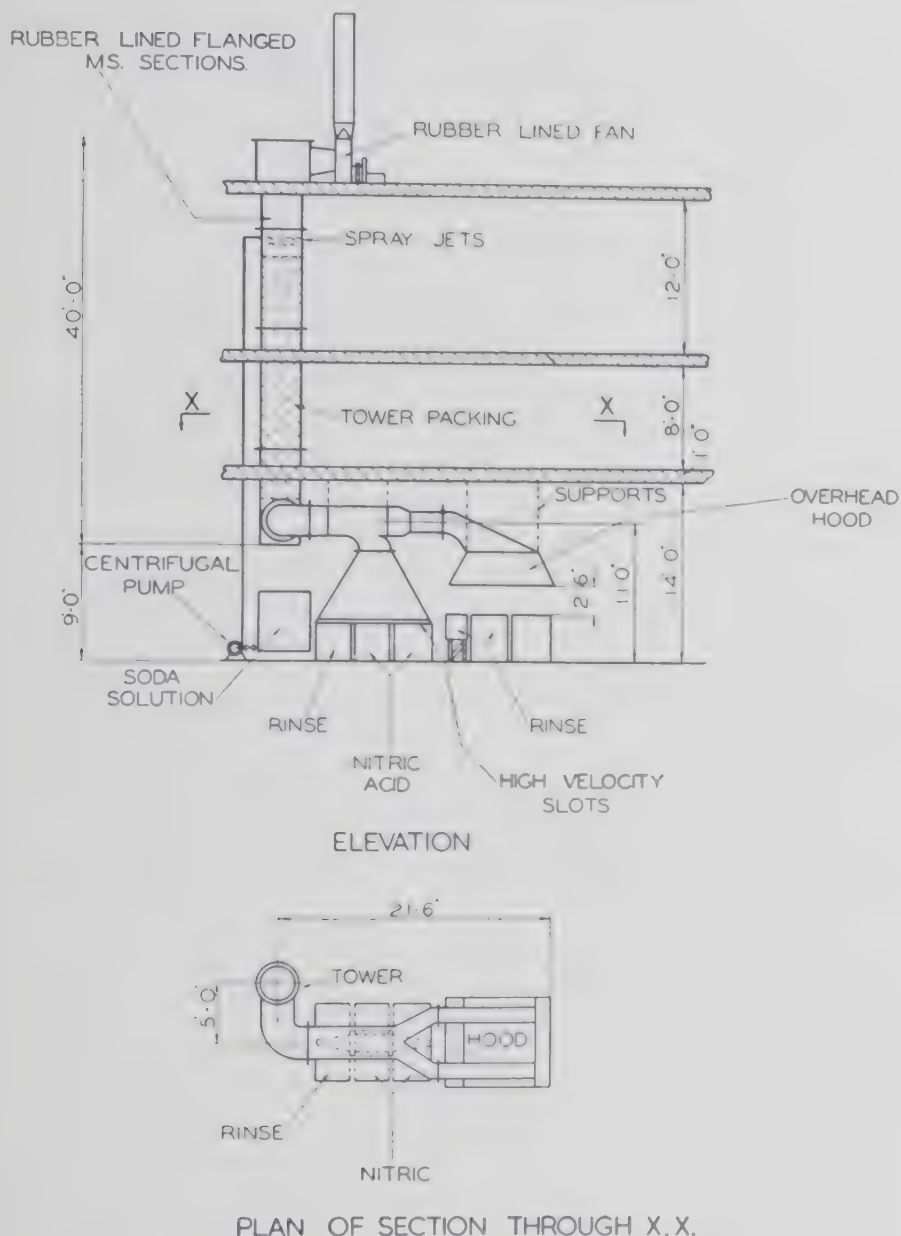


Fig. 23.—Diagrammatic section of fume disposal system for bright dipping plant

Nitric acid pickling of brass needs special care in washing as there is a tendency for acid to be retained in pores in the metal; this may ooze out later, especially if the metal is heated during lacquering operations, etc., causing "spotting" and discoloration.

To prevent tarnishing after bright dipping a useful technique is

to produce a thin soap film on the brass surface by dipping into a solution of about 1 ounce per gallon of cyanide, in which an ounce of neutral soap has been dissolved. The solution is kept slightly warm and the articles are immersed after thorough rinsing and then rinsed again. If proper rinsing is not obtained prior to immersion in the cyanide-soap mixture the latter will be precipitated on the work as a gummy fatty acid film.

The soap film protects the articles from tarnish for several days and does not interfere with subsequent electro-plating operations.

Fume Disposal.—Nitrous fumes from bright dipping tanks are heavy and are best exhausted from high-velocity slots extending across the dipping tanks. According to Mulcahy⁽³⁷⁾ the air velocity across the tank should be not less than 600 ft. per minute for every 12 in. from the slot lip to the opposite wall of the tank. Often the extraction fans exhaust to the air, but if possible the extracted air should be washed to remove the nitrous acid. To ensure scrubbing being effective the air speed should be reduced to 300 ft. per minute during the passage of the fumes through a scrubbing tower packed to three-quarters of its length with stoneware tower packing. A high-velocity jet spray ring is fitted to the top of the chamber for spraying soda solution, allowing a contact time of about two minutes. In this way the acid is neutralised and the alkaline solution can be discharged to the sewers periodically without further treatment. Fig. 23 shows the lay-out and construction of a typical plant for the removal and washing of nitrous fumes from a pickling plant for brass or copper.

The objectionable fumes generated when nitric acid is used in brass pickling and the danger of the acid being occluded in the pores of the metal has led to the use to some extent of other oxidising agents to replace it, in conjunction with sulphuric acid, in "bright dipping". One such solution employs sodium dichromate added to the extent of about 10 per cent to a warm dilute sulphuric acid solution. The rate of attack on the metal is increased by the presence of the dichromate, so that a brightened surface is produced. The solution may, however, etch the surface appreciably, especially on areas which may have suffered local dezincification during heat-treatment.

Ferric Sulphate. The use of ferric sulphate as an ingredient of pickling solutions used for stainless steels has already been referred to (see p. 47) and this compound is also finding increasing application in the pickling of brass.⁽³⁸⁾ The ferric ion is capable of oxidising copper to the soluble cupric state; thus acid ferric sulphate solutions

are able to dissolve the red cuprous oxide Cu_2O in the scale as well as the black cupric oxide CuO . These solutions have been successfully applied to most copper alloys, including brasses of all kinds, silicon bronzes, and nickel aluminium bronzes. The material is commercially available as the dry anhydrous salt, and is added to a 10 per cent sulphuric acid solution in the proportion of about 10 per

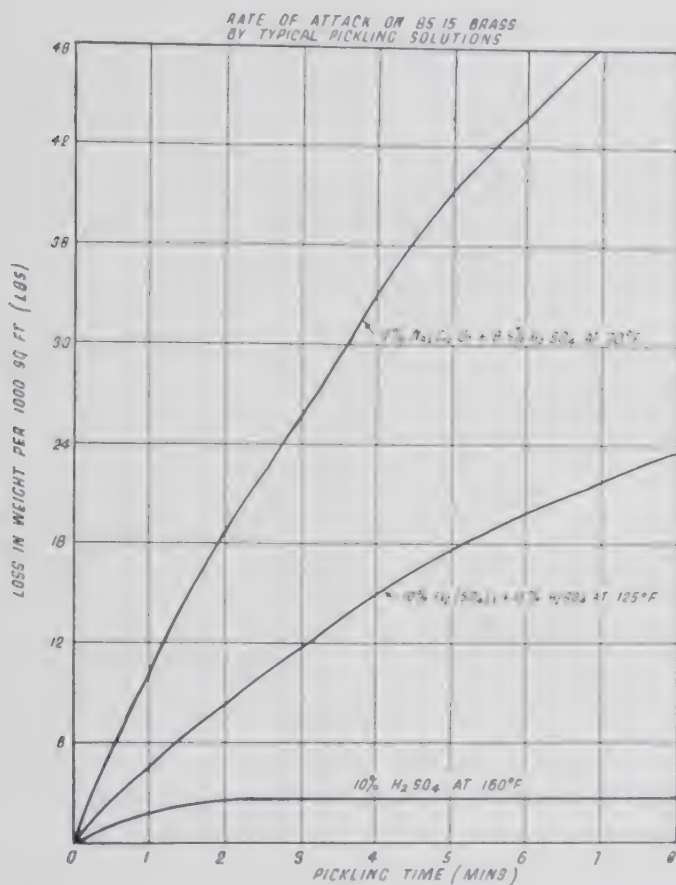


Fig. 24.—Rate of attack of pickling solutions on brass

cent, although the amount is not critical. The solutions are used hot, and short pickling times are employed. When the alloy contains beryllium or silicon the sulphuric acid may with advantage be replaced by hydrofluoric acid.

The ferric sulphate-sulphuric acid mixtures give a more uniform finish than does sulphuric acid alone. Although the appearance of the metal is not so light in colour as with the sulphuric-dichromate pickle, the rate of attack is slower and more uniform; there is thus

less etching of the metal surface. Fig. 24 shows the rate of attack on brass by various pickling solutions.

Normally, pickling in sulphuric acid-ferric sulphate mixtures does not produce a bright finish, but more recently additions have been introduced which enable brighter surfaces to be obtained. The finish is not as bright as that obtained from nitric-sulphuric acid mixtures, but is adequate for many purposes. Brightening baths which have been recommended for brass consist of a solution of 9 per cent ferric sulphate to which is added either 0.1 per cent cream of tartar, 3 per cent acetic acid, 0.5 per cent citric acid, or 0.5 per cent glycollic acid. The pickles are generally used cool, but in some cases a hot solution may be preferred. For nickel silver, 0.5 per cent of adipic acid was found to be the most satisfactory addition agent. By the inclusion of about 10 per cent of sulphuric acid in the solution a combined descaling and brightening bath can be obtained, which is useful in some instances.

Heat-resisting Alloys.—The pickling of the copper-nickel heat resisting alloys presents difficulty owing to the tenacious nature of the scale which is produced and to which these alloys owe their high resistance to oxidation when heated.

The descaling of Inconel (Ni 80 per cent, Cr 14 per cent, Fe 6 per cent) can be carried out in a nitric acid-hydrofluoric acid mixture. A recommended solution consists (by weight) of:

Nitric acid (67 per cent solution)	55 per cent
Hydrofluoric acid (40 per cent solution)	7 per cent
Water	Balance

An alternative procedure consists in pickling first in an alkaline sodium permanganate solution, followed by hot sulphuric acid at 70°C.

A rather slower solution, which has also been used, consists of 5 to 10 per cent hydrochloric acid solution containing 2 per cent of cupric chloride at a temperature of 70°C. to 80°C.

Electrolytic pickling has been employed, using 5 to 15 per cent of phosphoric acid at 50°C. Good results can be obtained by pickling this alloy in a solution containing 12 per cent of ferric sulphate and 3 per cent of hydrofluoric acid used at a temperature of 150°F. to 160°F.

Nickel-Chromium Alloys.—The nickel-chromium alloys (such as the 80:20 alloy used for resistance to high temperatures) are also very difficult to descale. The solutions in common use are similar to those employed for Inconel, but contain rather less nitric acid

and have a higher hydrofluoric acid content. A typical solution would contain (by weight):

Nitric acid (67 per cent solution)	30 per cent
Hydrofluoric acid (40 per cent solution)	20 per cent
Water	Balance

If the scale is not excessively heavy, a 3 to 5 per cent hydrochloric acid solution, containing 0.5 to 1 per cent of cupric chloride, can be employed. Other oxidising baths are not too satisfactory with nickel-chromium alloys; electrolytic pickling, using the phosphoric acid solution, has, however, been found more successful than with Inconel. Electrolytic pickling in sodium chloride solution is also effective, but tends to roughen the surface somewhat.

Ferric sulphate has been used very successfully in the pickling of this alloy, the best solution being one containing 6 per cent of hydrofluoric acid together with 20 per cent of ferric sulphate.

Mixed Metals.—A difficult problem in pickling is presented when a component consists of a variety of metals. The commonest of such cases is in the pickling of articles which have been brazed or soldered. Thus immersing steel articles which have been silver-soldered into sulphuric acid pickling solutions may result in the accumulation of copper salt in the latter, which will be re-deposited on the steel. There is no simple answer to this problem; every case must be treated on its merits, but, broadly speaking, if the acid is kept frequently renewed, assemblies of this kind can usually be pickled without undue difficulty.

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CHAPTER III

POLISHING

The polishing and grinding of metals often constitute an integral part of the finishing operation. In many instances the normal machined surface or the finish of sheet metals as they come from the rolls is satisfactory for the application of electro-deposited coatings or organic finishes. Thus, steel stampings are not commonly polished before zinc plating or spraying with paint, although acid pickling to remove scale may be necessary if the metal has been subjected to heat-treatment at any stage. For decorative finishes, such as bright chromium-plating and in most classes of work where a well-finished article is required, some degree of polishing is, however, necessary. There is also a not inconsiderable volume of evidence tending to show that a polished metal surface is likely to be more corrosion-resistant when subsequently electro-plated than an unpolished surface.

Broadly-speaking, the methods in use are:

- (a) Burnishing.
- (b) Polishing with abrasives, using flexible wheels, belts, discs, etc.
- (c) Barrel polishing or rumbling.
- (d) Electrolytic polishing.

Nowadays, burnishing is comparatively rarely employed, while barrel polishing is a method of producing a sufficiently bright surface especially on the cheaper type of article. The most general method of polishing in current use involves the use of flexible abrasive wheels in some form or another.

Burnishing.—By burnishing is meant a method of smoothing metal surfaces by flattening out irregularities by the application of pressure; the operation is carried out by means of a hard tool usually made of steel or sometimes of hard stone, such as agate or bloodstone. A considerable variety of tools are used in burnishing, which is especially suited to the softer metals, notably brass. The parts to be burnished are most often centred on a lathe and the pressure applied by means of the tool; flat articles can be burnished by hand. The tool must be kept highly polished, and for this purpose a suitable buff is employed dressed with burnishing putty powder.

During burnishing, the part is kept wet with a weak solution of

acetic acid (vinegar or ox-gall are also employed). Periodically the articles are dipped into cream of tartar solution to prevent tarnishing. They are left in the latter solution until they are ready for final drying off, which is accomplished by first dipping them into a solution of weak nitric acid or sodium cyanide to brighten the surface, after which they are washed and dried in hot water or sawdust.

Grinding.—Where a good finish is required, it is necessary to polish the articles by means of a suitable abrasive. If the metal is very coarse and much surplus metal has to be removed, a preliminary grinding operation must first be applied. A large variety of grinding machines are available, making use of solid grinding wheels horizontal, or vertical discs, etc. These may be used either wet or dry. Typical of grinding abrasives are *emery* (consisting essentially of alumina, iron oxide, silicates, and various impurities), which may be bonded together in the form of wheels, *artificial alumina*, which has largely replaced the dangerous silica abrasives, such as sandstone, and *silicon carbide*, a very hard abrasive made by fusing silica and carbon at high temperatures in the electric furnace.

After grinding has been carried out, if necessary, the metal is polished by means of wheels carrying abrasives held on their surface in various ways, as will be described later. •

Polishing Lathes.—Polishing wheels must be mounted on to a suitable lathe. The modern lathe for hand-polishing usually carries two wheels, driven by a single motor; the motor is preferably directly coupled to the spindle and, as a rule, carries a bearing at the end of the casing to provide extra support for the spindle. The polishing wheel proper is attached to the spindle either by means of a clamping plate passing over its threaded end, or, better, by making use of a taper-threaded spindle end on to which the wheel fits directly. This latter device is very rapid in use, and there is no need for any further fixing attachment, since the speed of the rotating spindle tends to force the wheel on to it. Changing of the polishing wheel is easily carried out.

The thread at the end of the spindle tends to wear in due course, so that detachable spindle ends are a very useful accessory, enabling the worn thread to be replaced quickly and cheaply. The method of attaching the wheel can also be altered from a taper spindle to a clamping plate very simply by removing the tapered spindle end.

The driving motor should be totally enclosed for protection against the ingress of dust, and the bearings should also be efficiently lubricated in such a way that polishing dust cannot find its way into them.

TABLE IX

RELATIONSHIP BETWEEN PERIPHERAL SPEEDS AND REVS. PER MIN.
FOR TYPICAL POLISHING WHEEL SIZES

Spindle revs. per min.	Wheel diameter				
	6 in.	8 in.	10 in.	12 in.	14 in.
Peripheral speed: ft. per min.					
1,000	1,575	2,100	2,600	3,100	3,600
1,200	1,950	2,550	3,200	3,750	4,400
1,400	2,250	2,950	3,650	4,400	5,100
1,600	2,550	3,400	4,200	5,000	5,900
1,800	2,900	3,800	4,750	5,650	6,600
2,000	3,200	4,200	5,250	6,250	7,300
2,200	3,450	4,550	5,750	6,900	8,000
2,400	3,750	5,000	6,300	7,500	8,800
2,600	4,100	5,450	6,800	8,200	9,600
2,800	4,400	5,900	7,400	8,900	10,500
3,000	4,700	6,250	7,900	9,400	11,000
3,200	5,000	6,650	8,400	10,000	11,800
3,400	5,250	7,000	8,900	10,600	12,500
3,600	5,600	7,500	9,500	11,300	13,200

The speed of the lathe is of importance, inasmuch as it affects the *peripheral speed* of the polishing wheel. Typical speeds are within the range of 5,000 to 9,000 ft. per minute. For the rougher polishing operations, it has been found that the lower range of speeds (of the order of 5,000 ft. per min.) can be used; these prove more economical than the higher speeds on grounds of wear and tear of polishing wheels and frequency of setting up. On the other hand, for fine polishing, speeds up to 12,000 feet or more per minute can be used with advantage. The relationship between peripheral speeds and revolutions per minute for some typical wheel sizes is shown in Table IX.

For the higher speeds it is desirable to use more concentrated glue mixes as the abrasive granules will need to be more strongly held. The linear speed at which different metals are most efficiently polished varies, the softer metals in general requiring higher speeds. Thus for stainless steel or mould metal 9,000 surface ft. per minute has been recommended, 6,800 ft. for brass, 6,000 to 7,500 ft. for aluminium, and 5,000 to 10,000 ft. per minute for zinc-base alloy die-castings.

In this country polishing lathes are not commonly provided with any means of altering their speed, although a two-speed counter-shaft or a three- or four-speed gear-box is occasionally fitted. In the U.S.A. variable-speed lathes are more widely used and present many advantages over the fixed-speed type. As the wheel wears down in diameter, the peripheral speed decreases if the number of revolutions of the shaft per minute is unaltered, so that poor polishing may result, owing to the drag of the slow-moving wheel.

In many of the larger polishing shops lathes are provided with



Fig. 25.—Disc-polishing of airscrew blades

[Courtesy of Sturtevant Engineering Co. Ltd.]

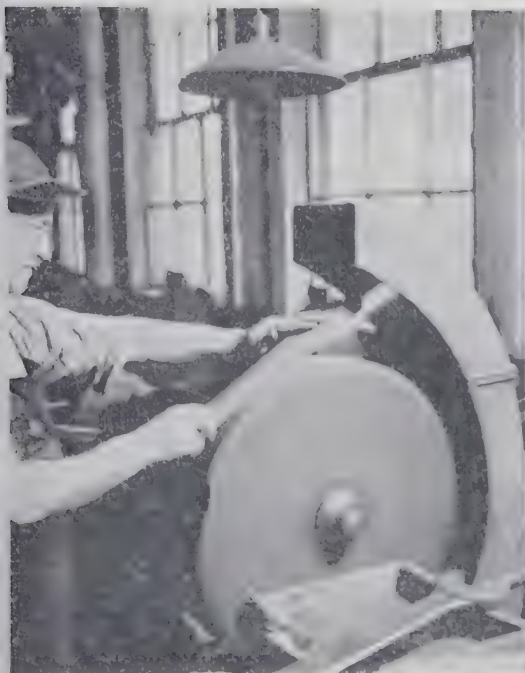
different fixed speeds, so that the correct peripheral wheel velocity can be more readily maintained for each size of wheel.

Some typical polishing operations are shown in the accompanying illustrations. Fig. 25 shows the disc-polishing of airscrew blades, whilst Figs. 26 (a) to 26 (g) show equipment used in the polishing of a variety of articles.

AUTOMATIC POLISHING

Nowadays, a great deal of metal polishing is carried out on automatic machines often designed for the polishing on mass-production lines of specific articles, such as motor-car handles, hub-caps, tubes, or metal sheet. A great deal of ingenuity has gone into the making of these machines. Their number is legion, and it would be impossible to describe many of them in detail here.

The automatic polishing and grinding of rods and tubes are



(a)



(b)



(c)

Fig. 26.

(a) Polishing edges of steel strips

(b) Polishing cultivator disc

(c) Polishing car bumpers

Figs. (a) to (e) and (g) by courtesy of Norton Grinding Wheel Co. Ltd.

Fig. (f) by courtesy of Sturtevant Engineering Co. Ltd.



Fig. 26 (d).—Polishing a guillotine knife blade

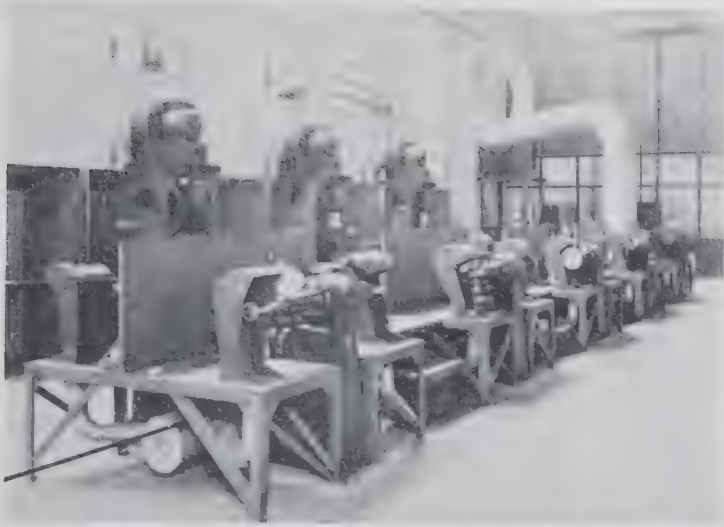


Fig. 26 (e).—Polishing the handle of a plantation hoe

accomplished in two types of machine. In the centreless polisher the tubes are passed between the polishing wheels by means of profiled feed wheels and suitable chucks; the rate and angle of feed and also the pressure applied during polishing are capable of fine adjustment. An alternative method is to make use of an abrasive-coated continuous band travelling over an inner cushioning band to control the pressure during polishing. Metal strip is regularly polished automatically; the strip is fed continuously through a series of pairs of vertical polishing wheels, when the metal is simultaneously polished on both sides. When the strip is in coil form, winding gear is incorporated at each end of the machine.

Sheet is also polished continuously in the same way as strip by mounting a series of polishing wheels side by side on a single spindle. The horizontal sheet is carried backwards and forwards on a reciprocating table, while the polishing wheels revolve at high speed. The spindle carrying the wheels is simultaneously subjected to a slow oscillating movement, as this helps to produce a good finish free from score marks. Machines of this type have been built capable of polishing sheets up to 6 ft. in width, and of considerably greater lengths.

An adaptation of the continuous strip machine is one designed for the polishing of flat-irons (Fig. 28). Here the parts are fed one after another under a series of polishing wheels. These are mounted independently, and are capable of movement in a vertical plane to enable them to keep in contact with the different levels as the flat-irons pass under them, while a lateral movement aids in the production



(f)



(g)

Fig. 26 (f).—Polishing wheels and dust extractors
(g) Polishing flutes of wood drills

of a uniform polish. This type of machine is capable of dealing with many types of components of relatively flat section.

One of the most successful types of machine for polishing the complicated shapes of automobile bumpers now in use in this country makes use of semi-automatic rather than fully automatic principles. The bars are held down on a table capable of oscillating to and fro. Two pairs of bars are polished at a time, using twin polishing wheels. The table carries one pair of bars forward under the

polishing wheels; a control lever then moves the traverse to the other pair of bars down which the wheels move. In order to complete the polishing of bumpers of deep cross-section, provision is made for the polishing wheels to move through a limited arc about a horizontal axis, whilst an oscillating movement can be given to the traversing table by hand at the same time; this substantially eliminates parallel marking of the bars. Power is conveyed to the large polishing wheels from motors mounted at the back of the machine by means of belts; the

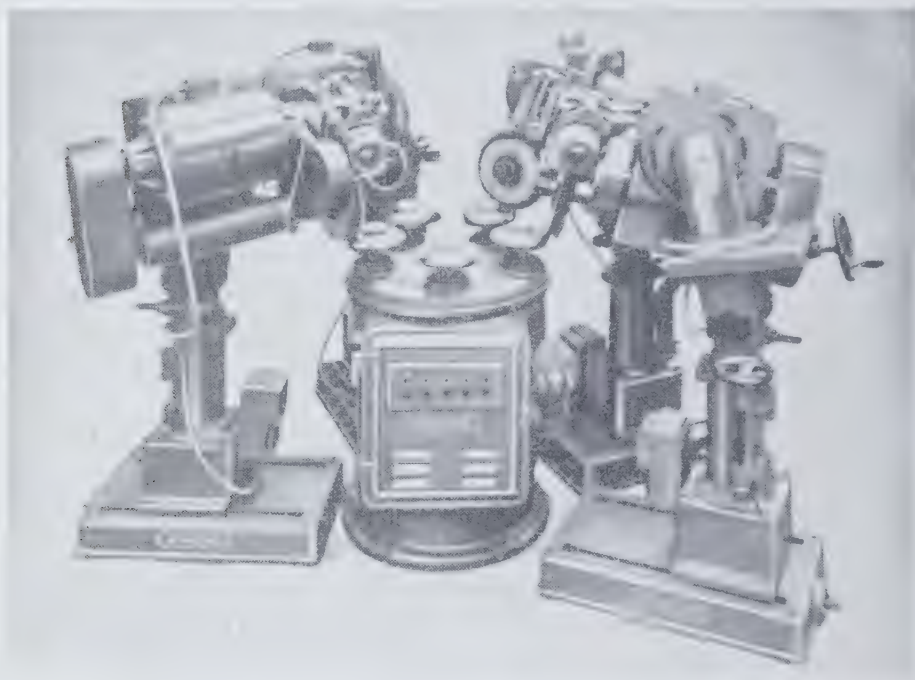


Fig. 27.—Five-spindle automatic polishing machine

arms carrying the wheels themselves are carefully counter-balanced so as to ensure that the correct pressure is applied in polishing. A recently developed American machine is worthy of mention; in this the bars are polished automatically on a circular rotating table, 18 ft. in diameter. In practically all automatic bumper polishing machines the ends of the bars must be hand-finished.

Multi-spindle Automatics.—Rotary polishing machines having an indexing device and a number of independent polishing heads have been introduced and are capable of giving good results. Fig. 27 shows a five-spindle automatic machine which can be arranged for either continuous rotation of the table or indexing for each spindle. Up to eight spindles can be accommodated for indexing.

To deal with a wide range of components, the polishing heads can be adjusted from a horizontal to a vertical position. All the heads can be fitted with an automatic feed for the polishing composition. The indexing type of machine can polish up to 250 components per hour of a maximum diameter up to $7\frac{1}{2}$ in.

The continuous table machine is limited with regard to the size of the articles it will polish, 1 in. being the maximum diameter, with a maximum length of 2 in. Outputs of 1,500 to 1,800 components per hour can be obtained.

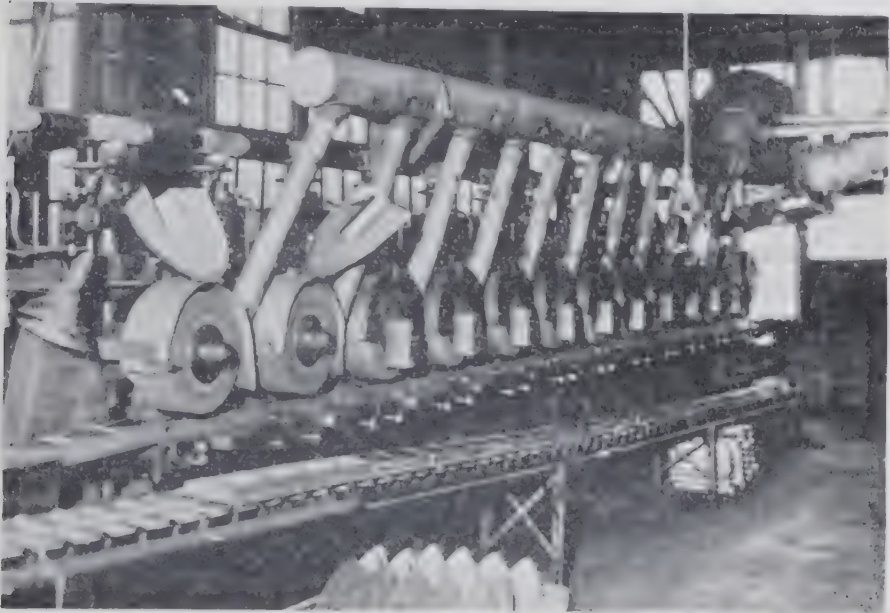


Fig. 28.—Polishing sole plates for electric irons on battery of machines using conveyor system. Polishing wheels vary from coarse for roughing to fine grit for finishing

(Courtesy of Norton Grinding Wheel Co. Ltd.)

Ring-shaped articles, such as headlamp rims and meter and clock bezels, are held in expanding chucks attached to revolving heads as shown in the machine illustrated in Fig. 29. The head moves intermittently, allowing the articles to be attached, after which they are automatically rotated and held against the two or more polishing wheels attached to the machine.

Knife polishing is carried out between large diameter (up to 24 in.) wheels rotating in opposite directions in a vertical plane. The wheels are brought together by means of a pedal, whilst the knife is held between them and pulled in and out slowly. At the same time a cam imparts an oscillating movement in a vertical plane to the knife.

For the polishing of difficult shapes, such as cycle forks, agricultural implements, hooks, etc., endless bands are used on suitable attachments. These are dressed with emery or other suitable abrasives in a similar manner to that employed in the case of polishing wheels, as will be described below. For other purposes portable wheels are used, and these can be attached by means of flexible shafting either to the end of a polishing spindle or directly to an

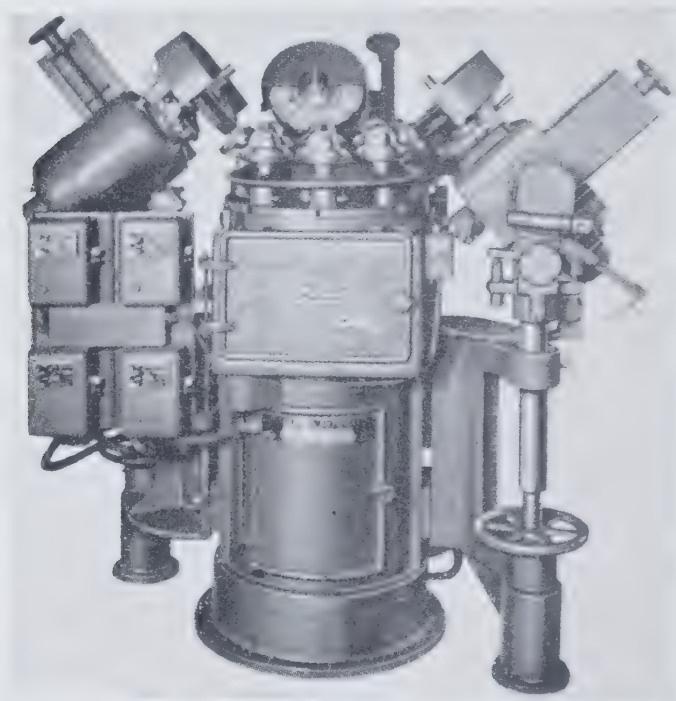


Fig. 29.—Rotary automatic polishing machine for small components

electric motor. Fully automatic polishing machines require that provision be made for the automatic application of the polishing compound to the wheel heads if uniform results are to be obtained. For solid compounds a motor or compressed air driven cam gear can be arranged to feed a predetermined amount of composition per revolution of the cam.

Liquid spray type of compounds are more readily applied, but have the disadvantage that the medium is usually inflammable; however, recent improvements in non-inflammable spray compounds indicate that these may find more extensive application in the near future.

The design and operation of automatic and semi-automatic machines have been described by Clements.⁽¹⁾

Advantages and Disadvantages of Automatic Polishing.

Machines of this type are used for the polishing of metals prior to electro-plating, and also for the buffing of the plated deposits. They are rapid in action, sometimes reducing the polishing time by as much as 90 per cent, as compared with that taken for hand-polishing. There are, however, certain features about automatic polishing machines which need careful attention if the best results are to be obtained. In the first place, they may not be capable of polishing all areas of parts of difficult shape, so that an additional hand-finishing operation may have to be applied subsequently. This will often represent a relatively costly proportion of the entire finishing process owing to the additional handling involved. Secondly, in order that polishing may be effective and to avoid jumping or chattering of the polishing wheels, there is a tendency for the pressures applied to be made substantially higher than those used by the hand-polisher. This, together with other effects, may result in a rather high rate of wear of polishing wheels in some cases. A third disadvantage of fully automatic polishing is that the machine is not able to "dwell" on local imperfections for the purpose of polishing them out. Semi-automatic machines enable such defects to be dealt with, on the other hand. High pressures are especially to be avoided in the finishing of nickel-plating where the removal of 25 per cent or even more of the nickel deposit in the finishing operation is by no means uncommon. Zinc-base die-castings should also not be polished too heavily prior to plating to avoid wearing through the dense surface skin and exposing the relatively porous interior of the casting. Furthermore, plated deposits will be disproportionately thinned at the point where the wheel first makes contact with the article unless very great care is taken at the commencement of the polishing stroke to ensure that the initial contact is made smoothly.

POLISHING WHEELS

Polishing wheels are made of a variety of materials, such as fabric, felt, leather, etc. Fabric wheels are built up of discs of canvas, calico, etc., clamped and sewn together. For rough polishing, and where any appreciable amount of metal is to be removed, the wheels employ "set-up" heads in which an abrasive is applied to the peripheral surface of the polishing wheel and held there by means of glue. (See p. 92.) A series of such wheels or "bobs" is employed for each successive operation, making use of a finer grade of abrasive on the head until a high enough degree of finish is obtained. The art of metal polishing involves the skilled use of a suitable cross-polishing

technique whereby the scratches left by the coarser polishing media are removed at each stage.

The next operation is carried out with buffing wheels (or "mops") without a set-up head on to which the polishing abrasive is applied by holding a stick of a suitable polishing composition against the buff whilst the latter is rotating at speed. Finally, for the highest finish, a "colouring" operation, using soft mops, is carried out with fine compositions, such as rouge, lime, etc.

The following are amongst the better-known types of polishing wheels as used in the industry.

Compress wheels are constructed from sections of canvas, leather, felt, etc., built on to the periphery of a wheel, which may be of steel or of wood. They are extremely durable and maintain their original shape and density for long periods. Their construction, since the discs of leather or canvas are held by side-plates, results in the absence of any need for glue or cement; the wheel presents no seams or joints, and only the endwise fibres are applied to the work in the direction of rotation of the wheel. The heading operation is, therefore, most readily carried out whilst the head itself is very strongly adherent. A great range of flexibilities can be obtained by the use of this type of wheel, which is also suited to the manufacture of wheels with "formed" faces. The compress wheel is, however, rather expensive, which is its main disadvantage.

Felt wheels are employed with the finer grades of abrasive, and are extremely flexible. They are used where a high finish is to be applied. They hold the abrasive well, and can be made into special shapes for dealing with intricate work.

Felt wheels are highly resilient and are fast-cutting. Their springiness makes them less liable to cause deep scratches than the harder wheels, so that they are very useful in "colouring" operations where some metal is to be removed leaving a lustrous finish. Felt wheels retain their shape very well and do not lose their contour. Solid felt wheels are the most satisfactory type because of their uniformity, but sewn or cemented felt discs are also often used.

Covered wheels consist of a wooden centre around which is placed a layer of leather or felt. The wood provides a solid backing, which makes this type of wheel especially suitable for polishing flat articles, such as knives and door plates. Thick leathers, such as walrus hides, bullneck leather, and other specially selected and tanned grades, are preferred for such wheels, because of their flexibility.

Walrus wheels, built out of solid hide (which is usually from 1 in. to 1½ in. thick), are used for small, highly flexible polishing wheels.

Walrus hide wheels can be obtained as single discs in thicknesses of up to $1\frac{1}{2}$ in., but for greater thicknesses several discs are cemented together. The porous nature of the hide gives it an altogether characteristic strength and resilience; these wheels are invaluable in the finishing of hardened steel parts, particularly in the cutlery and small arms industries. In the jewellery industry they are used in conjunction with abrasives suspended in oil.

Sheepskin wheels are highly flexible, and are employed for the polishing of the softer metals, such as brass and zinc and aluminium alloys.

Stitched canvas or calico wheels are very widely used for all types of polishing operations, because of their relatively low cost and high durability; they are exceptionally suited to the coarser grades of abrasive used for rough polishing. They may be used either with set-up heads (when they are known as "scurf-mops"), or for finer finishing, with compositions. Grease is often applied to set-up polishing bobs where a finer cutting action is required; this acts as a lubricant and tends to prevent tearing of the wheel surface.

Canvas disc wheels are used for rough polishing castings and forgings for parts for agricultural implements, stoves, plumbing fixtures, etc. The open weave of the canvas enables them to hold glued coarse abrasive heads very strongly. By using different types of stitching a widely varied range of flexibilities can be obtained.

Buffing Wheels.—*Buffing wheels*, or "mops", do not make use of glued heads, the polishing composition being applied to them from a bar of the latter, whilst the wheel is rotating.

Disc buffs are made from a number of discs of cotton, leather, etc., either held together in the centre to form a loose open wheel, or stitched together to give a harder type of buff. The former is used in the "colouring" of nickel, brass, steel, etc., whilst the stitched wheels are used for the "cutting down" of the softer metals.

Stitched piece buffs are made from off-cuts of material instead of from full discs of cloth. They are considerably cheaper than the full disc buffs. Various types of sewing are used on stitched buffs, including circular, spiral, tangential, and square sewing to stiffen the fabric and prevent distortion under pressure. The first two types are most common, and the closer the rows of stitches the harder is the wheel. Two types of sewing are shown in Fig. 30.

Folded buffs are more widely used in the U.S.A. than in this country, and are made up of discs folded into quarters, each of which is fitted successively into another quarter circle until a full wheel is built up. These buffs are said to have the advantage of holding the

polishing composition better and can be used for cutting when rotated in one direction and for colouring when run in the opposite direction. They are also better ventilated than the earlier types mentioned.

The *continuous strip buff*, the popularity of which is increasing in this country, makes use of a single bias-cut strip of fabric not more than half the diameter of the buff wound in a helix until the necessary thickness has been built up. As it is wound, the fabric becomes puckered at the outer edge to compensate for the difference between the inner and outer circumferences of the wheel. The result is that

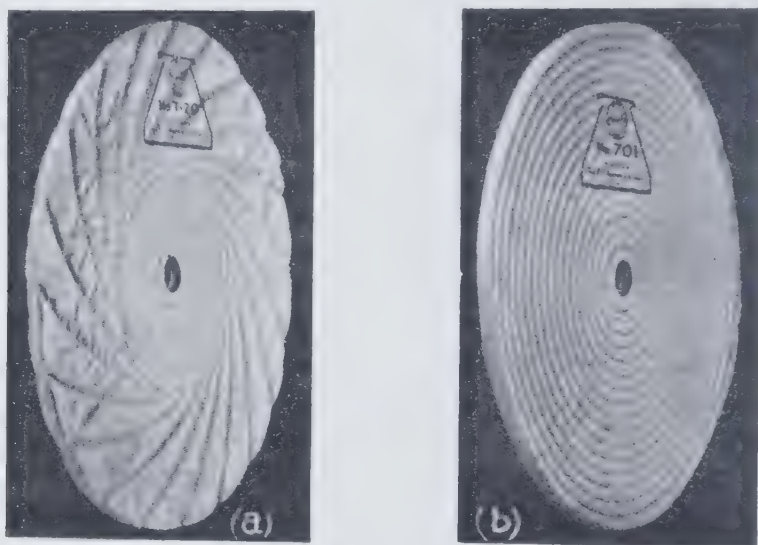


Fig. 30.—Stitched polishing buffs
(a) Tangential sewing (b) Spiral sewing

the edge of the buff is wavy. This has the advantage of minimising the appearance of polishing marks on the work. This wheel, like the last, is of the ventilated type, so that it can be used with higher pressures and at greater speeds than the conventional type of buff without burning or charring. Polishing is carried out more quickly, and the ventilated buffs are worthy of wider use. Moreover, there is no need for the wheels to be "rested" from time to time to allow them to cool, and they do not become overheated under normal working conditions. The method of construction of the folded and continuous strip ventilated buffs can be seen from Fig. 31.

Cotton buffs should be made of long staple cotton and of tightly twisted yarn. The more closely woven the fabric, the harder will

be the resulting wheel. In the stitched piece buffs the pieces should be laid on a bias relative to the periphery of the wheel, otherwise the shorter threads at the edge of the disc will be torn out. The wheel then tends to wear into a square section; such a wheel is weak and is liable to "bumping" in use.

Basil buffs are made up from sheepskin discs, and are employed for the colouring of brass, copper, etc.

Many other types of "mops", such as swansdown, chamois, and so on, are used for special finishing operations.

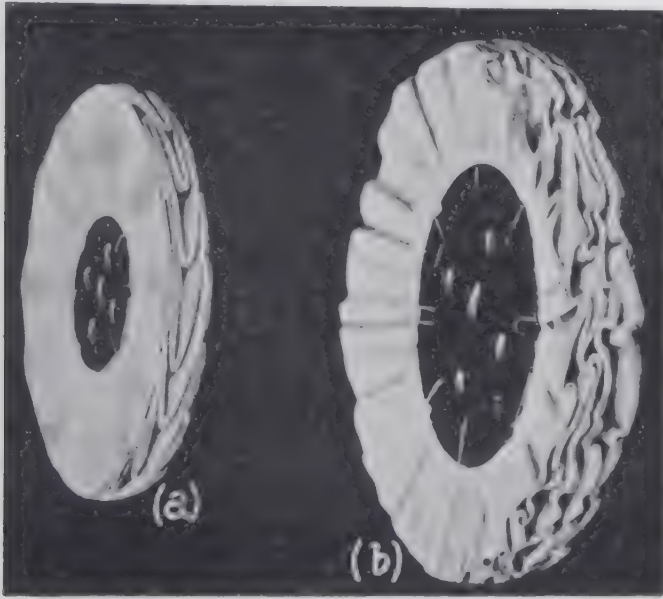


Fig. 31.—Ventilated polishing buffs
(a) Folded type (b) Continuous strip type

Abrasives and their Application.—The abrasives employed for rough polishing or buffing are of various types. Natural abrasives, such as emery, are used, whilst artificial aluminium oxide is being increasingly employed because of its hardness and because of the extent to which it is possible to control not only the grain size, but also the crystal form of the abrasive granules. The artificial abrasive powders are manufactured in such a way that they have a high surface capillarity in order that they may adhere well to the polishing wheel when the latter is glued and dressed with them. The range of particle sizes used in general polishing operations are around 60 to 90 mesh for ordinary roughing down, 120 for successive operations, after which the finest grades are employed for finishing operations. The latter are obtainable in grades down to 600 mesh. Uniformity of

particle size is of the utmost importance if satisfactory polishing free from scratches is to be obtained. Modern synthetic abrasives are also specially treated to ensure that they have the best capillarity to enable them to be firmly bonded by the glue. Capillarity is reduced by exposure to dirt or grease, and even exposure of the abrasive to the atmosphere for any length of time will noticeably reduce the strength of a polishing wheel head set up with it. Wheels dressed with a high-grade synthetic abrasive have an open type of coating with a clearance between the grains; the result is that the wheels do not fill so easily with metal particles from the articles being polished. For finish polishing such materials as tripoli, rouge, and chromium oxide find application; these are used in the form of blocks of compositions which are applied to the buffs in the dry state, whilst they are rotating. (See p. 97.) Siliceous polishing materials are to be avoided wherever possible, because of the health dangers arising from the dust which they generate.

Setting up of Wheels.—In setting up the polishing wheel, the latter is first painted with a glue solution and rolled in a trough containing the abrasive. The wheel is then dried out under suitable conditions.

Hide glue is most commonly used for the dressing of wheels. The glue is soaked in cold water overnight if slab glue is used, although ground or flake glue is to be preferred, since it only needs to be soaked for a much shorter time. It is then placed in a water-jacketed gluepot, which should preferably be thermostatically controlled at 160° F. If the wheel and the abrasive are heated before the application of the glue (as is very desirable) a lower glue temperature of about 140° F. is favoured. Glue loses strength when kept at temperatures above 160° F., and even at lower temperatures fresh quantities should be made up every three or four hours. The strength of the glue is determined by the amount of water used; with high-speed wheels a stronger glue is needed than is the case with lower speeds. Table X gives the glue strength commonly used under average conditions with various grades of alumina abrasive.

Before applying the glue to the periphery of the wheel the nap of the fabric is raised by running the wheel at high speed against a sharpened steel bar. This operation is also used for "contouring" the section of the wheel if it is to be used for the polishing of articles of special shape. Gauges are often used to facilitate the contouring operation. A short nap on the wheel surface helps to bond the abrasive, but if the nap is excessively long it will have an undesirably sharp cutting action. Finally the wheel is dressed with a

TABLE X
GLUE STRENGTH FOR ALUMINA ABRASIVE

Grain size of "Alundum" aluminium oxide abrasive	Glue per cent	Water per cent
24-36 . . .	50	50
46-54 . . .	45	55
60-70 . . .	40	60
80-90 . . .	35	65
100-120 . . .	33	67
150-180 . . .	30	70
220-240 . . .	25	75

carborundum stone to smooth the surface. The wheel is then ready for the application of glue or cement.

The hot glue is brushed on to the wheels in a warm room (about 80° F.) in order to prevent too rapid setting; the wheels are then rolled quickly and with even pressure in a trough containing the abrasive until the glue has picked up as much as it can hold. A second coat of glue and more abrasive can then be applied on top of the first if required. To avoid too early gelling of the glue, both the wheel and the abrasive grains are heated to 110° F. to 120° F. Too early setting of the glue lowers the adhesive qualities, and, moreover, the grains do not penetrate into the glue film so that the abrasive content of the latter is too low; the result is a slow-cutting wheel, which will tend to overheat.

Uniformity of grain size is important, as is also the shape of the abrasive granules. They must be solid and sharp-cornered to have the maximum cutting qualities. When wheels are being set up with different grades of abrasive the troughs should be placed sufficiently far apart to ensure that larger grains do not fall into the trough carrying the finer granules, or score-marks may result when the wheels are used in polishing operations. The usual types of grain troughs are relatively short and the abrasive must be rolled into the wheel a section at a time with a pounding movement. A recent innovation is the use of a long grain trough in which the entire wheel can be rolled in one continuous motion, using even pressure. The pressure used to pound the wheel into the grain must be uniform, and the actual pressure of application has a marked effect on the polishing action of the wheel. When the wheel appears dry and no glue can be seen, the process is complete.

Before redressing, wheels are trued by pressing a file against the surface whilst they are running at normal speed. Residual glue is then removed by means of an abrasive brick whilst the wheel is still running, and this also serves to raise a nap on the surface, to which the glue will adhere.

Polishing wheels should be run in the same direction at all times, with the lie of the nap.

Drying.—The next stage is the drying of the wheel, and this must be carried out under controlled conditions if the best results are to be obtained. Hide glue attains its maximum strength not when it has been completely dried, as is sometimes erroneously believed, but when it has a water content of 10 to 12 per cent. The drying-room should therefore be controlled both as regards temperature and relative humidity, so that the final moisture content of the glue approximates to the condition at which its strength is a maximum. The ideal drying conditions usually recommended are 85°F. and a relative humidity of 50 per cent.

The drying time depends on the thickness of the glue film containing the abrasive and the strength of the glue used (which in turn depends on the grain size of the abrasive, as shown in Table X). It may also vary to some extent with the size and nature of the material of which the polishing wheel is constructed. Under-drying weakens the glue, so that the wheel will tend to glaze, and will have poor cutting qualities. It is also likely to overheat in working, and may even catch fire. If the wheel is over-dried, on the other hand, the glue becomes unduly brittle, so that the abrasive granules tear out of the adhesive film easily, and the wheel has to be re-dressed after a short time.

Drying is generally complete in twenty-four to forty-eight hours under the conditions specified, the thicker-coated wheels naturally taking a somewhat longer time. The air in the drying-room should be circulated, and if additional humidification is required this can be obtained by means of a small electrically heated water boiler placed in the room; the heater is connected through a relay to a hair hygrometer with contact points attached to the needle, so that the heater is switched on and off between a range of, say, 45 to 50 per cent relative humidity.

In Great Britain it is, however, not generally necessary to humidify the air artificially, and sufficient control can be obtained by varying the temperature of the drying-room to obtain the required humidity. The graph (Fig. 32) shows how it is possible to obtain the optimum drying conditions within the drying-room from the temperature

and relative humidity of the incoming air. This chart is based on the assumption that good drying conditions are obtained when the vapour pressure of water in the room is 15 mm. less than the saturation vapour pressure at the same temperature. A recent innovation has been the use of "infra-red" or radiant heating units whereby it is claimed that the heads can be dried completely satisfactorily in an hour or two. The wheel is then balanced statically on a spindle and small dished counterweights can be nailed at a point on its side, if necessary.

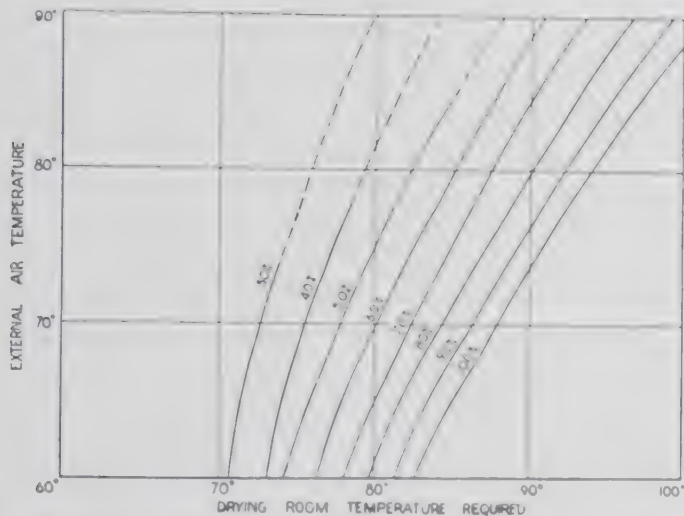


Fig. 32. —Drying of polishing wheels. Graph showing relation between external air temperature and drying-room temperature necessary for obtaining any required relative humidity. Temperatures are in degrees F.

Set-up fabric disc wheels must have their surfaces broken up to give them the necessary flexibility. The breaking of the head is done by striking the wheel flatly on the face with a round bar at an angle of about 45 degrees to its axis, going round the whole wheel two or three times. The process is then repeated in the opposite direction, so that the bar falls on to the face of the wheel at right angles to the direction of the first blows.

Cements.—The use of cold cements has become of increasing importance in recent years as a replacement for glue. Glue tends to soften with heat, but the cements are not subject to this effect so that the abrasive is more firmly held at high speeds. The drying of cemented wheels can also be carried out more expeditiously. Generally speaking, for the coarser abrasives the cements are more satisfactory than glue, and it is here that they find their chief application. For fine polishing, glue appears to be superior in most cases.

Abrasive Belts.—Abrasive belts of either canvas or leather are set up by coating them with glue in a manner similar to that described above, sprinkling the abrasive on to the surface and finally pressing it in with a wooden roller. An alternative method is to add the warmed abrasive powder to the liquid glue of appropriate strength until a paste is formed, which can then be spread on to the belt with a palette knife. The belts are finally dried under conditions similar to those employed in the case of polishing wheels. Occasionally, polishing wheels are dressed in the same way.

Sprayed Wheel Heads.—The usual methods employed for the setting up of polishing wheel heads described above are slow and laborious and some attempts have been made to improve on them. As polishing is something of a craft the introduction of new techniques has not been easy. Nevertheless, simpler and quicker methods of applying the abrasive to polishing wheel heads are leaving the experimental stage and are meeting with some measure of success in production, chiefly in the U.S.A. These methods mostly require the use of cold adhesives, which are based on silicates and have the advantage of drying at room temperatures, whilst their strength does not deteriorate on keeping as does that of hot glue. They will dry in air in about 12 hours, but better results are obtained by stoving at about 150° F. In operation cold adhesives withstand higher temperatures than does glue, although their holding strength for the abrasive granules is somewhat lower.

Whilst the abrasive granules can be applied to the cold adhesive in the usual manner by the trough method, it is also possible to incorporate the abrasive into the adhesive and apply the mixture directly to the polishing wheel by brush, or better, by means of a spray gun. Owing to the protecting effect of the adhesive it is sometimes advisable to employ a rather larger grain size than usual for the same degree of cut. Much thinner heads are used than in the normal procedure but it is claimed that wheels set up in this way last about five times as long as those headed in the common manner. These heads are especially suitable for obtaining satin or butler finishes.

A useful method employing these mixtures is to mount an air-operated spray gun on the hood of the polishing lathe with a pedal operated foot-valve. The operator is then able to spray a thin coating of abrasive on to the polishing wheel as required; this dries instantly and work need not be interrupted. This technique is very useful on automatic polishing machines where the buffs may be difficult of access so that considerable delay results when they have to be taken down and replaced. All kinds of abrasives can be applied in this

way including tripoli compounds for stainless steels, lime finish, emery and alumina. It is especially economical and results in a substantial saving of material, particularly where bar compound is used. In applying such compound to the buff a very substantial proportion is dissipated by friction and does not adhere to the wheel; by the spray technique, however, this loss is very largely reduced.

The method has its disadvantages, one of which is the difficulty of maintaining a uniform dispersion of the abrasive in the adhesive. Another, and perhaps more serious objection, is the fact that the sprayed abrasive system cannot be used in conjunction with a grease finish owing to the fact that the water-soluble adhesive will not adhere to grease. As grease is almost essential where high mirror finishes are required, the spray application of abrasive has tended to be confined to the coarser polishing operations. The difficulty can be overcome by the use of organic solvents, such as kerosene, as the carrier medium, but this introduces a serious fire hazard. Recent developments in emulsion type abrasive suspensions have shown promise, however, so that the method may find more extensive use than has been the case hitherto, since the emulsions are non-inflammable.

Polishing Compositions.—A considerable variety of polishing compositions is available to the industry, most of them being proprietary products developed as a result of considerable experience by the makers. They consist of abrasives bonded together with a grease base, which melts when the composition in bar form is held against the rotating buff; in this way a small amount of abrasive is held by the surface of the wheel. The grease is helpful in some cases in producing a smooth finish, but often its presence is undesirable. For this reason greaseless compositions have lately been developed and are of increasing importance.

Greaseless compositions are mixtures of glue and abrasive and are easily applied to all types of wheels. They are especially useful in dealing with articles such as stampings from which all imperfections cannot readily be buffed out with grease compositions. Compositions are employed in buffing operations as distinct from polishing, and no abrasive is held in the polishing wheel head. Buffing is used where only a very small amount of metal is to be removed in order to obtain a smooth surface. It precedes the final "colouring" operation whereby the highest lustre is obtained. The buffing wheels are generally of unbleached calico held together by various types of stitching.

A good composition should adhere to the polishing wheel just so long as the abrasive retains its cutting qualities and no longer. It

should also be economical in use, clean off readily in operation and be easily removed in the cleaning solutions used prior to plating.

The abrasives used are materials such as tripoli powder, diatomaceous earth, green chromium oxide, emery, etc. Lime compositions (made of calcined dolomite and containing a high proportion of magnesia) are extensively used for finishing electro-plate and as a last operation prior to plating, since they serve to remove grease residues from previous operations, thus helping the plating process. The best-known grades are Sheffield or Vienna lime. They are sometimes applied to the buff in lump form, but are more often used in the form of "white composition". Green oxide compositions are useful in putting a high finish on to stainless steel and also on chromium-plate. Synthetic alumina is often an important constituent of polishing compositions, because of its excellent cutting qualities and because the grains retain their abrading edges for a long time.

Emery is a natural form of alumina, which, however, contains considerable quantities of ferric oxide and impurities. The finest grades are known as emery flours and are used where high finishes are required. Tripoli powder is a finely divided silica of diatomaceous origin and a very common ingredient of polishing compositions.

Tripoli compositions provide a fast-cutting abrasive suitable for producing a high lustre on non-ferrous metals. Where a considerable amount of cutting down is necessary a greasy composition is used, with a drier grade for lighter work, since the grease holds the abrasive on the wheel longer.

Abrasive Belt Polishing.—A development which is fast becoming more widely used is the method of abrasive belt polishing in which the polishing wheel is used simply as a base for an abrasive belt which runs around it and is supported at its remote end by a Back-stand Idler. The wheel itself may be of any suitable resilient material. Sometimes an ordinary canvas mop is used, or one made of a suitable grade of rubber will often prove very satisfactory. A typical back-stand unit is shown in Fig. 33.

This system has the advantage that factory-produced belts can be used which are uniform and cool running, whilst the skilled work of setting up and drying polishing wheels is entirely eliminated. It is, however, a method which is best used for rough polishing as the belts lack the flexibility for dealing with finer polishing operations, on intricate parts especially.

The Art of Polishing.—Metal polishing is still in many respects an art, and it is difficult, if not impossible, to lay down general

rules. Peripheral wheel speeds must be selected to give optimum results, not only from the point of view of the appearance of the finish, but also to ensure that due economy in labour and materials is being obtained. The appropriate wheel of the correct flexibility must be selected for each job. Care should be taken in the handling of the article to prevent sharp edges meeting the polishing head and causing the latter to wear unduly quickly.

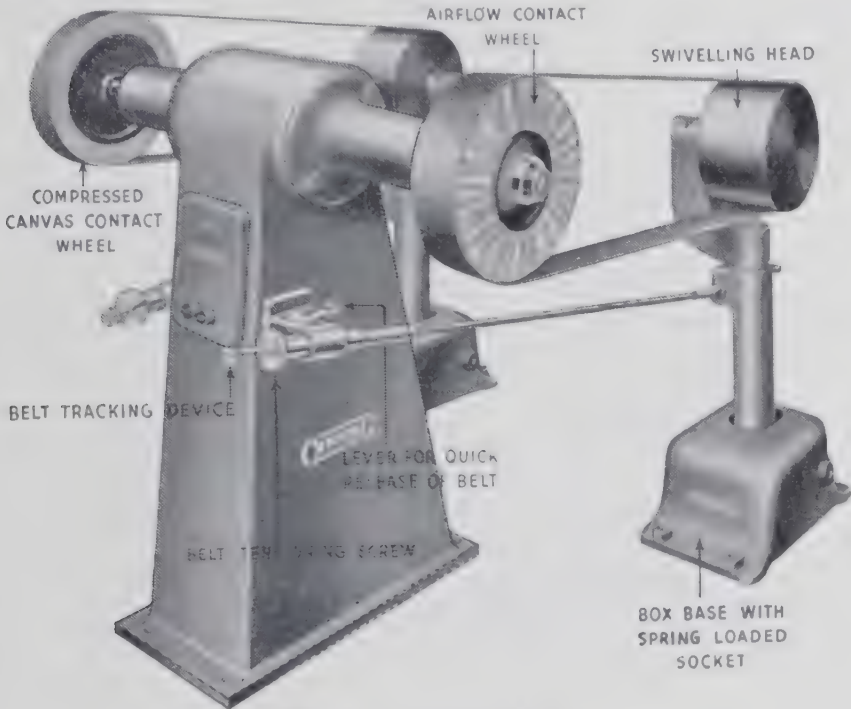


Fig. 33.—Back-stand idler

The different grades of polishing are termed “roughing”, “greasing”, “finishing”, etc., depending on the cycle of operations used. For roughing a fairly coarse abrasive is used on a dry wheel, but for the finer polishes grease or compositions are applied to the wheel. The lubricant not only helps in the production of a smoother and brighter finish, but also prevents loading or glazing of the abrasive head and reduces discoloration by preventing the wheel from overheating. The polishing wheel life is therefore also considerably increased. Lubrication is particularly helpful in the case of the softer metals such as aluminium and zinc-base alloys.

The observations of Pinner⁽²⁾ on the influence of the direction of rotation of the polishing wheel with respect to the direction of movement of the work are significant. Grinding and deep cutting for

removing surface imperfections and polishing scratches are carried out by moving the work in the opposite direction to that in which the wheel is rotating. It is important, however, that the final polishing operation just prior to plating should be accomplished with the work moving in the same direction as the rotation of the wheel when polishing steel prior to nickel-plating. In this manner, microscopic steel slivers are removed, and the absence of such particles definitely favours the production of smooth deposits which are more easily buffed and will possess improved corrosion resistance. The final wheel should also be a partly used one to reduce the tendency for scratches to appear to a minimum.



Fig. 34. Lay-out of polishing shop for hand finishing motor-car handles
[Courtesy of Sturtevant Engineering Co. Ltd.]

The following are some typical polishing cycles for a number of metals. The initial grade of abrasive used in each case depends, of course, on the condition of the metal surface. If the surface is good, the coarser polishing operations can be omitted. Where emery is recommended it can with advantage be substituted by the corresponding grade of synthetic alumina.

Aluminium.—Polish with a greased felt wheel and 90 emery, followed by 120. Next use a tripoli composition on a stitched mop and finish with an open cotton buff with lime composition.

Steel. If the surface is very coarse, roughly polish with emery of 60 mesh on canvas wheels, followed by 90 and then 120 on greased cotton bobs. For subsequent nickel-plating an improved surface can be obtained by finishing with levigated alumina on an open mop.

Stainless steel.—Polish with 90 alumina, cross-polishing to remove scratches. Follow with a white composition on a cotton buff, and then finish with a chrome oxide composition. Emery should not be used on stainless steel, as the particles of iron oxide present may become ingrained in the metal surface and promote corrosion.

Speeds of 6,000 to 8,000 ft. per minute are recommended for grinding and polishing. Stainless steels have low thermal conductivity so that they are easily overheated. For this reason excessive pressures during the polishing or buffing operation must be avoided.

Zinc-base alloy die-castings can be polished with 120 emery on the parting "flash" of the casting only, then buffed with a stitched mop, using tripoli composition. It is desirable to have as high a finish on the die as possible. This reduces the amount of polishing to a minimum and so avoids the danger of polishing through the surface "skin" of the casting. Fig. 34 shows the lay-out of a shop for the hand-polishing of zinc-base die-cast motor-car handles.

Nickel-plate is polished direct on cotton mops with lime composition.

Chromium-plate can be "coloured" on a Basil mop, either with a white composition or, if the deposit is very dull, with green oxide composition.

Dust Extraction.—Dust extractors are essential on polishing equipment. Careful design of extractor cowls and duct-work is needed to ensure that there is a minimum of bends and constrictions in the latter, and that the positioning of the former does not interfere unduly with the handling of the work. Automatic machines present special problems; in one installation where a very large amount of dust was generated a successful solution was found by putting each machine in a compartment of its own, and extracting air at high speed through a water curtain at the back of the compartment. A running water floor also served to prevent dust accumulation. The same water was pumped around continuously, the accumulations of sludge in the water being filtered out on wire mesh screens.

BARREL POLISHING

Barrel polishing provides a very cheap method of finishing metal parts, such as castings, stampings, forgings, and many kinds of small parts, which require the removal of burrs, etc. Accurately machined components and parts threaded externally are not suitable for barrelling.

The operation is usually carried out in two stages; in the first stage the parts are scoured to remove roughness, protuberances or

scale, after which they are given the final polish in a second barrel.

It must be stressed that barrel finishing is an operation which demands special consideration in the case of each type of article being polished; the best conditions in every instance can often only be determined by actual experiment.

The barrels used are of various types, including horizontal closed barrels, or open-inclined barrels, which are usually employed for

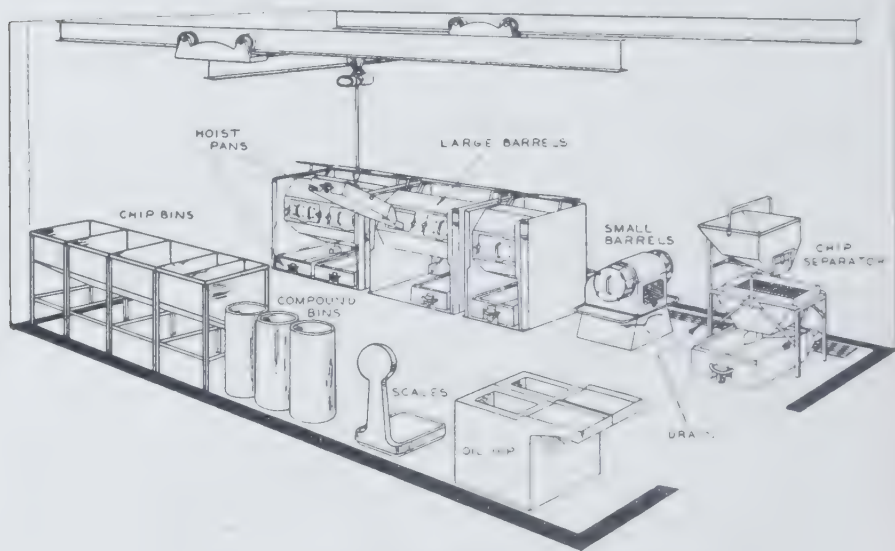


Fig. 35.—Lay-out of barrel polishing shop

final brightening and drying in sawdust. The barrels may be circular in section or polygonal and made of wood, steel, cast-iron, plastics, or rubber-lined metal. Wood barrels should be of beech or oak, and are often reinforced with metal. Resin-containing softwoods are undesirable. Hexagonal or polygonal barrels give a better cutting action than circular barrels because of the accelerated fall of the parts as they drop successively from each face of the barrel as it revolves. They are, however, best avoided for the initial scouring of softer metals. The barrel speed varies, the higher speeds (of the order of 200 ft. per minute) being used for light articles, while heavier components are barrelled at speeds down to half this rate.

Sometimes the container is given an oscillatory motion in addition to the rotary movement. This helps polishing and prevents nesting, but the wear on the bearings of this type of barrel is very heavy.

Scouring.—For scouring, the parts are put into the barrel together with materials such as scrap pieces of steel of suitable form (e.g. tube ends, flats, stars, etc.), steel balls, and an abrasive which may be aluminium oxide, sand, granite chippings, rottenstone, etc. For the final polishing, less aggressive abrasives, such as diatomaceous earth and putty powder, are employed. Either paraffin (or mixtures of paraffin and oil) or water may be added to the polishing barrel as a carrier. The former is extremely useful, especially on steel; but if water is employed the presence of a small amount of alkali is desirable in order to prevent rusting.

Two sizes of steel balls are best used together when hollow parts are being treated; the larger size is then able to deal with the outside surfaces, while the smaller balls reach the interiors. Steel balls must be protected from rust when not in use by storing in soapy water.

Although it is practicable to remove scale in the scouring process, the hardness of the oxide deposit makes this somewhat difficult. It is therefore advisable where possible to degrease and pickle scaled articles prior to barrel polishing. This applies even more strongly to parts which have oil burnt on to them, as a result of annealing (notably those made of brass). Such components should be degreased prior to annealing if the best results are to be obtained. Barrels used for scouring iron or steel parts should not be used for softer metals, to avoid damage to the latter by any harder metal particles that may be left in the barrel. If it is desired, however, to use a barrel which has been employed for steel parts to finish zinc, for example, it should be thoroughly washed out with paraffin to remove any iron particles that may remain inside.

As an example a suitable mixture for the barrel polishing of small steel or brass parts would consist of: (i) powdered rottenstone; (ii) a mixture of equal parts of oil and paraffin; (iii) steel scrap or balls if necessary. The parts being polished should not constitute more than about 50 per cent of the total mixture.

As a general rule, barrels are run about two-thirds full. Soap is included in the mixture to maintain a foam when non-ferrous metals are being treated, as it is found that this is conducive to a bright finish. Excessive soap concentrations are best avoided as they reduce the cutting action, although they may, at the same time, improve the lustre of the finish at the cost of a longer barrelling time.

On the question of barrel speeds, the barrels can run up to 30 revolutions per minute; speeds in excess of this are impracticable as undue damage to the articles being treated will result. For parts

weighing up to 2 lb. 24 r.p.m. is a useful general speed; higher speeds result in a centrifugal action, causing excessive impingement and damage or complete locking of the mass so that no polishing action occurs at all.

The components are packed in the barrel in such a way as to avoid nesting. The barrel is filled to within a few inches of the top, since if too much space is left they will be damaged during the polishing operation. The barrel is closed and run for a few minutes, after which it is reopened. It will then be found that some settling has taken place, and more parts are then put into the barrel to fill up the space. The time of polishing may be of the order of two to six days, depending on the nature of the parts being treated and on the finish required.

When the operation is complete, the barrel is emptied into a sieve, where the oil drains off; the parts are then separated by hand. When non-ferrous metals are being polished, the steel scrap, balls, etc., used as polishing assisters can be removed by means of a magnet. Ferrous parts can, with advantage, be dipped in a rust inhibiting, or de-watering oil after treatment.

The purpose of the detergent in barrel burnishing is to keep the metal clean and remove metal particles from pores in the abrasive which tend to clog it. Such clogging substantially reduces the cutting power of the abrasive.

The proportion of abrasive stone to parts has been worked out by Wingate⁽³⁾ on a basis of the "box" volume of the components, i.e. the volume obtained by multiplying together the three longest linear dimensions of the parts concerned. The resulting figure is a theoretical box sufficient to enclose the part concerned. Table XI gives the data for a wide range of component sizes, unsymmetrical in shape and up to 2 lb. in weight.

The abrasive must be changed at intervals, as it loses its sharpness. The oil-paraffin mixture can be used for longer periods, being thinned with paraffin from time to time.

Final Polishing (Barrel Burnishing). After scouring, when a higher degree of polish is required, the parts are removed from the barrel and are degreased or washed in paraffin and put into a finishing barrel. If any tarnishing has occurred, it may be necessary to pickle lightly for a few minutes in 5 per cent sulphuric acid, or, if the parts are of a copper alloy, to clean them in a dilute cyanide solution.

The finishing barrels must be kept clean and free from grease or oil. The barrel is filled with a solution containing soap-flakes,

TABLE XI
RECOMMENDED RATIO OF PARTS TO ABRASIVE FOR
BARREL POLISHING

"Box" Volume of Parts [cu. in.]	Stone to Part Ratio	
	Ferrous	Non-Ferrous
up to $\frac{1}{4}$	1 : 1	may be self- tumbling
$\frac{1}{4}$ to $\frac{1}{2}$	2 : 1	1 : 1
$\frac{1}{2}$ to 1	5 : 1	2 : 1
1 to 2	8 : 1	3 : 1
2 to 3	10 : 1	5 : 1
3 to 4	13 : 1	7 : 1
4 to 5	15 : 1	8 : 1
5 to 6	18 : 1	10 : 1
6 to 12	25 : 1	12 : 1
12 to 20	35 : 1	15 : 1
20 to 30	45 : 1	17 : 1
30 to 50	55 : 1	20 : 1
50 to 100	100 : 1	25 : 1

preferably with the addition of a small amount of sodium cyanide to act as a brightener. Trisodium phosphate is also a useful brightening addition agent. In any event, the solution must be kept well on the alkaline side if the best results are to be obtained. Into the solution, together with the parts being polished, are put small steel balls, together with material such as steel scrap and leather cuttings. Small wood blocks are also useful (as a filling material, rather than as a polishing agent), whilst rosin-free sawdust (boxwood and beech dust) are sometimes added. Limestone chips are a specially useful constituent when a high lustre is required. The parts should constitute some 30 to 50 per cent of the contents of the barrel. The barrel is filled completely, and is run for a few minutes, after which it is opened and more filling material (such as wood blocks) added to prevent excessive damage to the parts when the barrel is rotated. The polishing operation should be complete in six to twelve hours, after which the parts are removed and transferred to heated open sawdust barrels, in which the final drying and polishing is completed in about five minutes; they are then ready for the subsequent plating or other finishing operation.

A special problem in barrel polishing is presented by soft metal parts with a harder metal insert. Thus, motor-car handles are made of zinc-base alloy, into which a steel shaft is often cast. Such parts cannot be barrelled in the conventional manner, as the steel shafts would damage the soft zinc. By holding the handles in the interior of the barrel in suitable fixtures they can, however, be successfully polished. The loading of such a barrel is a slow process, whilst its capacity is naturally somewhat limited. An alternative method which has been proposed is to protect the steel shafts by some sort of soft covering such as a rubber sleeve.

Unlined hexagonal steel barrels running on a horizontal axis tend to be favoured nowadays. The technique of barrel polishing has also been improved by the introduction of specially made artificial abrasive stones, sometimes consisting of a matrix of a soft abrasive material in which particles of harder abrasive are embedded. These abrasives are available in a range of sizes and hardness for different types of finish and for different sizes and shapes of articles. By methods such as these, articles can now be barrel finished which would formerly have been considered as quite unsuited to this method of polishing.

Fig. 35 shows the lay-out of a modern barrel polishing shop designed for ease of working.

ELECTROLYTIC POLISHING

Electrolytic methods of polishing metals have aroused considerable interest in recent years, both on account of the reduction in cost and in labour which they are capable of bringing about, and also because of the fact that in some instances it is possible to produce a higher degree of finish than is obtainable by mechanical methods of polishing.

Beilby⁽⁴⁾ pointed out that when metals are polished mechanically, a thin superficial layer of amorphous material is produced which has lost its crystalline structure (the so-called Beilby Layer). More recent work⁽⁵⁾ shows that this layer is about 20 Å. to 40 Å. thick, and below this is a further micro-crystalline layer before the normal structure of the metal is reached. It is considered that this surface layer is produced by the local heavy pressures and high temperatures produced during mechanical polishing operations, which cause the surface layer of the metal to flow.

Jacquet⁽⁶⁾ investigated methods for polishing metals for metallographic examination which would be capable of producing a smooth surface without distorting the crystal lattice, which is an inevitable concomitant of the formation of a Beilby Layer. He found that it

was possible to obtain a high degree of polish on steel specimens by making them anodic in various electrolytes, such as a mixture of perchloric acid and acetic anhydride. It was found that copper could be polished to produce surfaces more highly reflecting than those resulting from mechanical polishing methods. The copper was made the anode in a solution containing about 400 gm. per litre of phosphoric acid or pyrophosphoric acid at a temperature of 15° C. to 20° C. under carefully controlled conditions of current density, location of anodes, etc.

The perchloric acid-acetic anhydride mixtures give better results on steel, but the critical influence of differences in the type of steel and even the method of heat-treatment, coupled with the nature of the chemicals used (the mixture can become explosive under some conditions), makes it very difficult to apply the process to commercial articles.

Mechanism of Polishing.—The action which takes place in the electro-polishing bath occurs as a result of the highly polarised conditions prevailing at the anode. During treatment a film is produced which may be gaseous or liquid, in the latter case usually a layer of solution containing a high concentration of salts of the anode material. If this film has a high resistance to the passage of current, and the surface consists of depressed and elevated areas, it is clear that the thickness of such a film will be greater in the depressions so that the current density will tend to be high on projections and low in the protected depressions. The high current density areas will thus be dissolved away so that the entire surface of the metal will tend to be flattened and evened out. Polarisation effects may also come into play which tend to make the depressions relatively anodically passive and the elevations anodic due to differences in the concentration of the anodic film.

Racking.—Parts to be treated must be separately racked; the time of treatment is about 5 to 20 minutes. Slight agitation is helpful, but must not be excessive. The main object of movement is to prevent streaks due to the passage of oxygen bubbles over the parts being treated. Racks are best protected by means of an insulating lacquer or coating, but pure copper racks can be successfully used in the uninsulated state with many of the stainless steel electrolytes as the metal becomes passive after a few seconds and does not dissolve.

Stainless Steel.—The advent of the stainless steels (especially the austenitic types which came into extensive use in sheet form) provided a useful and practical application for electrolytic polishing methods. Stainless steel is most difficult to polish mechanically;

high pressures must be applied, and the low thermal conductivity of the metal makes overheating of the polishing wheels liable to occur. Good polishing is essential in the case of the austenitic steels, and overheating or a poor finish are likely to result in a surface of low corrosion resistance which is liable to pitting or rusting in service.

It has been found that stainless steel can be polished anodically in a variety of acids, apart from those already mentioned, of which sulphuric-phosphoric and sulphuric-citric acid mixtures are the most effective and simplest to apply in a commercial sense, being relatively free from difficulties of operation and from obnoxious fumes.

The phosphoric-citric acid bath consists of 55 to 60 per cent of citric acid, 15 per cent sulphuric acid, and the rest water. It is maintained at a temperature of 185° F. to 200° F. The solution has a relatively long life, and low current densities can be employed. During electro-polishing the metals removed are converted to sulphates and precipitate out of the bath to some extent as a sludge. This is removed from time to time. The use of a small amount of methyl alcohol in this bath has also been advocated.

In some experiments carried out by Young and Brytczuk⁽⁷⁾ it was found that of the phosphoric-sulphuric acid mixtures, surfaces of highest reflectivity were obtained when the steel was made the anode in a solution of 60 per cent phosphoric acid, 20 per cent sulphuric acid, and 20 per cent of water. The bath was run for three minutes at an anode current density of 5 amps. per sq. in. and at a temperature which did not exceed 80° C. The presence of water aids the electrical conductivity of the solution and reduces the voltage necessary for polishing. On the other hand, an excess of water permits the sulphuric acid to etch the steel chemically, thus impairing the brightness of the finish. Considerable heating of the solution occurs and cooling coils must be introduced into the tank; excessive rise in temperature causes etching of the steel. The method is applicable to iron and carbon steel, as well as to stainless steels, but better results are obtained with the latter, since, in the case of carbon steels, there is a greater tendency for chemical etching to occur, especially at the crystal boundaries of the metal. It seems probable that the phosphoric acid in the solution results in the formation of a film of viscous metal phosphates in close proximity to the surface. This film protects the minute recesses on the anode from dissolution under the influence of the current, while ridges and protuberances above the general level are preferentially dissolved. Hence a smoothing of the surface occurs. Gradual diffusion of the film

takes place, however, so that the entire surface also tends to dissolve gradually. Other acids, such as perchloric and hydrofluoric acids, act similarly.

Organic materials, such as glycerin, have a favourable effect on anodic polishing,⁽⁸⁾ lowering the critical current density below which the insulating viscous film cannot be maintained. They also serve to minimise the chemical etching of the metal surface by the acid. The critical current density is important in electrolytic polishing, since if it falls below the minimum the diffusion of the anodic film proceeds at a faster rate than that at which it can be maintained. For this reason it is important to avoid excessive agitation or movement of the electrolyte and also to avoid the setting up of convection currents as far as possible. Current densities in excess of the minimum have no adverse effect even when they are relatively high. This is useful, since it makes the process applicable to parts of involved shape where wide variations in anodic current densities are to be expected. The addition of sulphuric acid to the phosphoric acids tends to reduce the chemical action on the steel, and also increases the rate of anodic dissolution, thus facilitating the polishing action.

Carbon Steels. Generally for satisfactory results carbon steels must be free from local defects or pits, as these tend to be increased in depth and emphasised by electro-polishing methods. For smoothing ground or polished surfaces electro-polishing can be helpful. Thus, a 50-micro-inch finish can be brought down to 40 micro-inches or less, whilst by starting even with a 5-micro-inch finish some improvement can be effected. The sulphuric-phosphoric acid electrolyte is applicable to carbon steels, and is normally operated at current densities of 100 to 500 amps. per sq. ft., and at temperatures as high as 190° F. Slow movement of the work in the bath is desirable.

For mild steels it has been found by the author⁽⁹⁾ that a solution with a wider operating range can be obtained by the use of cresol sulphonic acid in place of sulphuric acid in the sulphuric-phosphoric acid type of solution. The optimum conditions were as follows:

Phosphoric acid (sp. gr. 1.75)	160-180 pts. by wt.
Cresol sulphonic acid (sp. gr. 1.41)	130-150 pts. by wt.
Water	25-45 pts. by wt.
Current density	300 amps./sq. ft. minimum
Temperature	40°-60° C.
Time of treatment	5-15 minutes

The cresol sulphonic acid solution is not a well-defined material and is prepared by the sulphonation of 160 parts by weight of commercial cresol with 180 parts by weight of sulphuric acid (sp. gr. 1.84) and using the resulting compound direct.

Gentle mechanical agitation of the solution is necessary during working of the bath to prevent stratification.

In some tests carried out on finely machined rods 1 in. long by $\frac{3}{8}$ in. diameter, it was found that for a wide range of operating conditions a good polish could be obtained in fifteen minutes. The amount of metal removed under these conditions is shown in Table XII.

TABLE XII
REDUCTION IN DIAMETER OF MILD STEEL RODS BY ELECTROLYTIC
POLISHING

Current density amps./sq. ft.	Bath temperature °C.	Mean reduction in diameter (in.)
290	40	0.0013
370	40	0.0013
290	60	0.0021
530	60	0.0027

De-burring can also be carried out by this method, but the cost of racking, etc., may be prohibitive. The amount of metal to be removed may also lead to excessively frequent renewals of the solution.

Faust also describes a sulphuric-phosphoric acid bath containing a certain amount of chromic acid for the polishing of carbon steels and also some alloy steels. Very high current densities are employed (up to 1000 amps. per sq. ft.) together with high temperatures. The chromic acid is reduced to the trivalent state during working, so that the solution becomes greenish in colour; when the trivalent chromium content becomes too high (in excess of about 3 per cent), the operation of the bath is adversely affected. The solution is generally controlled by means of a hydrometer, and is discarded when the density becomes too high.

The use of this solution involves extraction equipment since chromic acid spray is evolved during its operation. A potential of 12 to 15 volts is required and may be supplied by generators or rectifiers.

Copper and Brass.—Jacquet has described the electrolytic polishing

of copper and brass, using a 53 per cent solution of pyrophosphoric acid as the electrolyte. The current density was 8 to 10 amps. per sq. dm. with an applied voltage of 1.6 to 2. The temperature was maintained at 15°C. to 22°C.

Orthophosphoric acid solutions have also been employed, solutions of 25 to 60 per cent concentration having been found to give good results. Similar current densities can be employed, the bath being operated at room temperature. A voltage of about 2 volts is generally adequate. The solutions seem to work better when some ageing of the electrolyte has occurred. The presence of a certain amount of copper in the bath stabilises the voltage and enables more uniform polishing to be obtained. The articles should be removed from the bath before the current is cut off, or copper may be re-deposited on the metal surface as a result of a back e.m.f. being set up. Sometimes a white deposit is left on the polished surface; this can be removed by immersion in a dilute solution of orthophosphoric acid.

The process developed by Faust⁽¹⁰⁾ makes use of a phosphoric-chromic acid electrolyte; a typical solution contains:

Chromic acid	50 per cent
Phosphoric acid	10 per cent
Water	40 per cent.

The composition of the solution and the operating conditions can be varied widely, but the best results are obtained at current densities of about 500 amps. per sq. ft. and temperatures of 100°F. The polishing time varies naturally with the state of the surface, but 5 to 10 minutes is generally sufficient. This solution may be used for the electro-polishing of copper or brass.

A sulphuric-phosphoric-chromic acid electrolyte has also been patented by Faust⁽¹¹⁾ which is capable of polishing copper, brass, nickel, steel and a wide range of alloys. The preferred composition is:

Phosphoric acid	59 per cent
Sulphuric acid.	4 per cent
Chromic acid	0.5 per cent
Water	36.5 per cent.

The operating conditions are similar to those for the solution free from sulphuric acid.

Baths containing chromic acid deteriorate rapidly, however, as trivalent chromium and copper accumulate in the solution, and when 2 to 4 per cent of these materials are present the solutions cannot be

used. Faust has therefore developed a solution for polishing copper which is claimed to last indefinitely, any copper in excess of 0.5 to 1 per cent being plated out on the cathode.⁽¹²⁾ Two solutions are recommended of which the first has a slightly higher anode efficiency:

	I	II
Phosphoric acid . . .	75 per cent	82 per cent
Trivalent chromium . . .	0.8 per cent	0.5 per cent
Trivalent aluminium . . .	0.3 to 0.6 per cent	0.4 per cent
Divalent copper . . .	0.3 to 0.5 per cent	0.4 per cent
Water	Balance	Balance

The solution can be prepared by dissolving the theoretical amount of aluminium in the aqueous phosphoric acid by heating. The trivalent chromium salt is added as chromic chloride, and the solution heated to expel the chlorine as hydrochloric acid, after which the water is added to the required level.

The solution is maintained by determining phosphate, chromium and aluminium from time to time. Stainless steel cathodes are employed. Current densities of 100 to 150 amps. per sq. ft. are used, the temperature of the bath being 100°F. to 130°F.

The use of trivalent chromium in the bath is not essential, but it facilitates the use of high current densities.

Various other solutions have been recommended from time to time for the electrolytic polishing of brass but the composition of the alloy influences the results obtained with particular baths to a considerable extent. Free-machining brasses containing lead are especially difficult.

An important problem with electrolytically polished brass arises when the metal is to be nickel-plated, as a passive film is left after treatment so that the plated deposit has very poor adhesion. Drastic treatments to remove this film cannot be applied without destroying the polished surface. One method of overcoming the trouble is to plate a very thin iron layer on to the brass from a suitable electrolyte prior to nickel-plating. Nevertheless, the commercial application of electrolytic polishing to brass has great possibilities and small-scale production is already being carried out both in this country and in the U.S.A.

The application of anodic polishing to the finishing of *nickel-plate* has been proposed by Hothersall and Hammond.⁽¹³⁾ The electro-plated article is made the anode in a solution of sulphuric acid under controlled conditions until a bright surface is obtained. The amount of nickel dissolved is relatively small.

Electrolytic Brightening of Aluminium.—Perhaps the most generally employed present application of anodic polishing methods on a commercial scale is in the manufacture of aluminium reflectors, which are electrolytically brightened on a large scale. Aluminium, when polished mechanically, even with the greatest care, has a reflectivity of only 65 to 75 per cent in the visible spectrum range, but by electrolytic polishing this can be increased to 80 to 85 per cent in the visible range, and even higher in the infra-red region. Mechanical polishing of aluminium seems to result in a flowing of the metal surface under the buff, preventing the development of a truly planar surface; the reflectivity is thus lowered.

The aluminium (which should be of high purity for the best results) is first polished with a felt bob dressed with 140-grade emery, and is then buffed on a stitched mop with tripoli; it is finally finished on a swansdown mop with tripoli. White composition and lime should not be used, as they may scratch the surface. It is then ready for electrolytic brightening. The best-known commercial processes are the Brytal⁽¹⁴⁾ and the Alzak⁽¹⁵⁾ processes. The former makes use of an alkaline brightening bath consisting of a solution of sodium carbonate and trisodium phosphate maintained at a temperature of 165° F. to 190° F. The parts are first put into the bath and suspended from the anode rod without current for a period of ten to thirty seconds, during which time a rapid evolution of hydrogen takes place. The duration of this etch must be carefully controlled, and the exact time depends on the purity of the aluminium. A potential of 10 to 14 volts is then applied for a period of five to eight minutes, when brightening takes place; the initial current density is in the range of 10 to 15 amps. per sq. ft., after which the current falls to about half this value. One of the troubles encountered in the operation of this process is pitting of the aluminium, which tends to occur particularly at higher voltages. It is claimed that the addition of very small quantities of sodium octyl sulphate will entirely prevent such attack.⁽¹⁶⁾ Apart from preventing pitting, the octyl sulphate also seems to permit the use of slightly higher current densities.

In the Alzak process various acid electrolytes may be used for anodic brightening, that commonly employed being fluoboric acid. Fluoborates and other special constituents may also be present. The solution is worked in a rubber-lined tank fitted with copper cooling coils which serve as the cathode. The temperature and current density are carefully controlled, and the cathodes are screened with flannel to prevent movement of the solution in the vicinity of the anode by gas evolution. The time of treatment is ten to fifteen minutes.

After removal from the electrolyte the aluminium is immersed in a hot alkaline solution to remove the polarised film left on the metal surface by the fluoborate treatment.

In both processes the brightened surface is subsequently given an anodic oxide film to provide a hard and durable reflecting surface. (See p. 430.) This anodic film is of the transparent type and in the "Brytal" process is applied in an electrolyte consisting of a 25 per cent solution of sodium bisulphate; the potential used is about 12 volts, the duration of the anodising treatment being twenty to thirty minutes. The Alzak process makes use of a sulphuric acid electrolyte for producing the anodic film.

The parts are then lifted from the anodic bath, and are placed in hot distilled water for a period of about twenty minutes to remove traces of electrolytes. It is found that after the treatment a very thin film is left on the metal surface, which can be removed by rubbing with whitening powder or better by immersion in a solution of 10 per cent sulphuric acid for about five minutes at room temperature. The reflectors are then dried in sawdust or in hot air. The film is finally given a sealing treatment by immersion in a boiling solution of cobalt acetate or by the application of lanolin in white spirit or a wax polish.

Table XIII shows some reflectivity figures for aluminium treated by the Brytal process as compared with other reflecting surfaces.⁽¹⁷⁾

TABLE XIII

REFLECTIVITY CHARACTERISTICS OF SOME REFLECTING SURFACES

Specimen	Total reflectivity per cent	Specular (parts in 100)	Diffuse (parts in 100)
Polished commercial aluminium .	73.1	93.1	6.9
"Brytal" on commercial aluminium	76.8	86.2	13.8
"Brytal" on "A" reflector aluminium	82.4	96.25	3.75
"Brytal" on super purity aluminium	84.1	99.4	0.6
Stainless steel	59.5	97.0	3.0
Chromium-plate	63.0	99.7	0.3
Rhodium on nickel-plate . . .	69.1	99.55	0.45
Lacquered silver-plate	89.9	96.5	3.5
Silvered glass mirror	90.3	(almost specular)	wholly

The total light reflected is expressed as a percentage of the incident light and the proportion of specular and diffuse reflection in the total is expressed in parts per 100.

Silver.—Silver can be electrolytically polished by anodic treatment in a bath of the same general composition as is used for plating. One solution which has been recommended consists of:

Silver (as $\text{KAg}(\text{CN})_2$)	.	.	4 to 6 oz. Tr./gall.
Potassium cyanide	.	.	4 to 5 oz. Tr./gall.
Potassium carbonate	.	.	6 to 8 oz. Tr./gall.

A voltage of about 5 volts is applied, the current density being of the order of 12 to 18 amps. per sq. ft. The polishing time is fifteen to twenty seconds.⁽¹⁸⁾

General Remarks.—There can be little doubt that electrolytic polishing methods have a considerable future. The electro-polished surface is usually free from strain, whilst the technique enables a variety of surface finishes ranging from a fully bright to a satin or matt finish to be obtained. Owing to the good “throw” of the solutions it is also possible to polish in recesses and at depths not normally accessible to mechanical polishing wheels. A surface does not need to be plane for a mirror finish to be obtained on it by electrolytic methods.

On the other hand the use of electro-polishing methods under commercial conditions introduces complications which have not yet been fully surmounted. The high current densities usually employed necessitate large sources of current; racks and conductors must also be of generous dimensions. The racks themselves must be insulated effectively owing to the destructive action of the solutions used under anodic conditions. These solutions are, as a rule, themselves highly corrosive to tanks and equipment. The heating and cooling equipment often needed are also subject to very severe conditions, and available materials of construction are not yet fully satisfactory in all respects.

Adequate surface finish, smoothness and the cleanliness of the surface have their effects on the polish obtained and on the economics of the process. Deep scratches, dirt and metallic or non-metallic inclusions should be removed prior to treatment by mechanical means for the most satisfactory results. The use of protective lacquers or coatings in pressing or drawing operations is often effective in reducing the tendency for marking to occur. Attractive finishes can also be produced by shot-blasting prior to electro-polishing, whilst two-tone effects can be produced by partial stopping-off during treatment.

A reasonable degree of cleanliness of the metal is desirable before immersion in the electrolyte, although a chemically clean surface is not essential.

Scope of Electro-polishing.—In a recent review⁽¹⁹⁾ Faust and Graves are at pains to point out that although industrial electro-polishing has been in use for over ten years there are many finishers who still expect electro-polishing to be another way to produce the burnished appearance of mechanically polished work. Such an accomplishment is impossible by the electrolytic process, yet electro-polishing produces a distinctive and acceptable appearance. Results are dependent on uniformity of grain size, homogeneity of structure and freedom from seams and non-metallic inclusions in the metal. Fine grain metals give the best results, hence electro-deposited metals give the best finish when electro-polished. No satisfactory method has yet been developed for the polishing by this method of zinc-base alloy die-castings or lead-containing copper alloys.

It is not possible to give any general data as to the relative costs of electro-polishing and mechanical polishing, as every class of work has to be studied individually in relation to the finish expected and the methods employed.

Chemical Polishing.—An offshoot of electrolytic polishing is the process of chemical polishing which is still in its early stages of development. In this process no current is applied, the articles being immersed in solutions of acids such as phosphoric, nitric and acetic. The temperatures used range from room temperature to as high as 200° F. for the fastest action. Solutions have been developed for the treatment of brass, nickel silver, Monel metal, nickel and aluminium. Chemical polishing of the latter metal in alkaline solutions is not new and has been used for many years in the Brytal process (q.v.).

The advantages of a non-electrolytic process are obvious, inasmuch as it can be used on intricately shaped articles or in barrels, whilst the difficult problem of racking is substantially overcome.⁽²⁰⁾

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DEGREASING AND CLEANING

The removal of oil, grease, and other contaminating foreign matter is an essential preliminary before almost any industrial finish can be successfully applied to metals. Such cleaning presents a formidable problem, which must be coped with, and it is probably true to say that the greatest single cause of finishing defects is poor cleaning of the metal surface.

The types of surface contamination which have to be removed can be broadly classified as follows:

- (a) Oils, greases, soluble oils, drawing compounds, lubricants and the like left on the metal surfaces, subsequent to mechanical operations such as rolling and pressing.
- (b) Polishing residues, which may include greases, soaps, abrasives, abraded metal and textile material from polishing buffs.
- (c) Metal swarf, grit, and also dust deposited from the atmosphere.
- (d) Tarnish and rust films developing during storage or handling.

The removal of scale resulting from heat-treatment is a somewhat different problem, and has been dealt with in Chapter II.

Lubricants.—The first group of materials mentioned above constitutes a major source of contamination. It is essential to use lubricants in most metal-forming and fabricating processes, and these lubricants contain a large variety of constituents. Besides mineral oils, vegetable and animal oils and fats are often present, as are greases, which may be of either the lime or soda-based types. Sometimes, for special purposes where very high pressures are employed, fillers such as zinc oxide are included in the compositions, whilst insoluble metallic soaps such as metallic oleates or naphthenates may be present in the form of extreme pressure lubricants. Ordinary alkali soaps are also employed to a considerable extent. When it is borne in mind that all these materials may exist on metals that must be subjected to a cleaning operation, and that many lubricants are of a proprietary nature, the constituents of which are not readily known, the magnitude of the task is realised.

The composition of a lubricant is governed almost entirely by effectiveness for the particular mechanical operation for which it is required. Generally speaking, scant attention is given to the problem of removing it for any subsequent finishing processes which may

have to be carried out, although it must be said that some few manufacturers of pressing and rolling compounds have given substantial attention to this aspect of the application of their products. Certainly it is one which merits research.

Types of Contaminants.—Broadly speaking, the oily contaminants on metal surfaces are of two groups—viz. saponifiable and non-saponifiable oils. The former are found in the largest amount in the animal and vegetable fats, which consist essentially of the salts formed by the combination of a long-chain fatty acid and an alcohol generally polyhydric, such as glycerin.

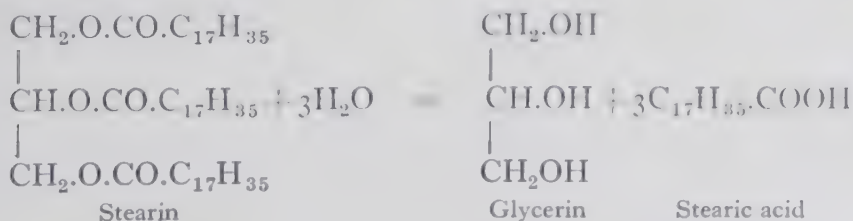
The animal fats are most commonly solid at room temperatures and consist largely of the glycerides of palmitic and stearic acid. On the other hand, the liquid vegetable oils contain a much higher proportion of oleic acid glycerides. Nowadays, considerable amounts of the liquid fats are converted to the more valuable hard fats by hydrogenation in the presence of catalysts such as finely divided nickel.

The chief constituents of the hard fats are tristearin and tripalmitin, which are, in fact, formed by the reaction of the glycerin, which acts as a tri-hydric base, with the corresponding fatty acid. Triolein is formed similarly by the combination of oleic acid with glycerin. Some of the properties of the fatty acid constituents in natural fats and oils are shown in Table XIV.

TABLE XIV

Fatty acid	Composition	Melting-point C.	Sp. gr. at melting-point
Lauric acid . .	$C_{11}H_{23}.COOH$	43·6	0·875
Myristic acid . .	$C_{13}H_{27}.COOH$	54·0	0·862
Palmitic acid . .	$C_{15}H_{31}.COOH$	62·0	0·853
Stearic acid . .	$C_{17}H_{35}.COOH$	69·0	0·845
Oleic acid . .	$C_{17}H_{33}.COOH$	14·0	0·854

When fats are heated with water under pressure or with sulphuric acid, hydrolysis takes place, so that the fat is resolved into glycerin and fatty acid. Thus:



In actual practice, when natural fats are hydrolysed in this way, mixtures of fatty acids present are obtained.

When alkalis are used in place of water, hydrolysis occurs very much more rapidly, and alkali salts of the fatty acid are produced, together with glycerin. These salts constitute the common soaps, and the process of boiling fats with alkalis to produce such soaps is termed "saponification", or, better, hydrolysis. So far as cleaning processes are concerned, the main aspect of interest is the fact that, whereas the oils and greases are insoluble in water, the sodium and potassium salts of the fatty acids formed by the action of alkalis on fats are entirely soluble. Thus, saponification by alkalis of such oils and greases effects their speedy removal. It is to be noted, however, that the soaps of alkaline earth metals, e.g. calcium (or lime) soaps and the magnesium soaps are not soluble to any extent in water. These are precipitated from the soluble soaps when hard water containing calcium and magnesium salts is used, and the removal of these insoluble salts which may be precipitated on the metal surface can present difficulties.

On the other hand, the mineral oils which are very widely used in engineering processes are substantially non-saponifiable. To this group belong petroleum jelly, lubricating oils, paraffin waxes, etc. These can be removed by means of organic solvents or by treatment in alkaline solutions, making use of the detergent, as distinct from the saponifying, characteristics of these materials.

There are three groups of substances used in metal cleaning and degreasing—viz.: (a) organic solvents; (b) detergents consisting of aqueous solutions of various materials, usually alkalis, with various additions; (c) emulsified cleaners.

ORGANIC SOLVENTS

Greases and oils are soluble in organic liquids such as benzene, naphtha, carbon tetrachloride, trichlorethylene, paraffin, petrol, etc., and grease removal can be effected by washing in these solvents. The ideal solvent for metal cleaning should meet the following requirements. It should be: (a) cheap and readily available; (b) non-inflammable; (c) an effective solvent for all types of oils, greases, waxes, and tars; (d) substantially non-toxic; (e) of low viscosity and surface tension to facilitate effective penetration of greasy deposits; (f) readily separable from the extracted matter with a high percentage of recovery; (g) non-corrosive to metals even at elevated temperatures. It is difficult to meet all these requirements, but some solvents approach them much more nearly than others.

The procedure of washing parts in a bath of cold liquid solvent has, however, several disadvantages. First, a film of the solvent containing a greater or less amount of oil in solution is left on the work; when this evaporates, a certain amount of the contaminant remains on the parts being cleaned. Secondly, the action of the solvent used in a cold, still bath is apt to be relatively slow, necessitating the use of large equipment. It also involves much handling and manipulation of the parts being cleaned.

Although a certain amount of rough cleaning is still carried out by washing in paraffin, solvent naphtha, or other inflammable solvents, this procedure is nowadays largely confined to the removal of accumulations of grease, mixed with considerable amounts of grime. Under conditions where efficient modern industrial degreasing plants using high-powered non-inflammable solvents are available there is little to be gained by the use of methods of this kind.

Emulsion Cleaners.—The difficulty of removing organic solvents from a metal surface, when they have accumulated any quantity of oil, has resulted in other attempts being made to find mixtures which will be capable of dissolving the oils and then be readily emulsified, so that both the cleaning agent and the grease can be removed by washing with water. These degreasing agents are either brushed over the articles to be cleaned, or the latter are immersed in the emulsion, or sprayed with it, after which the residue is washed off with water. The solvent and the grease which it has taken up are emulsified by the water, leaving the work in a clean condition. The emulsion is best used hot or warm.

One such combination which has been suggested consists of a mixture of one part of triethanolamine oleate with four parts of trichlorethylene, the triethanolamine soap acting as the emulsifying agent. Other suggested constituents of similar mixtures which consist essentially of a solvent soluble both in oil and water, together with a water-insoluble solvent, include dioxan and glycol monobutyl ether. Emulsion cleaners do not appear to remove water soluble contaminants if they are covered with grease or oil so that there is a tendency for corrosion to occur after cleaning in such cases. A more recent development which is claimed to have advantages in this respect is multiple phase cleaning. This type of cleaner consists of an upper layer of plain solvent and a lower layer of an emulsified aqueous solvent. The solution is best used in a spray washing machine with the pump intake in the lower phase. By this method powdered iron, for example, which is not readily wetted by the emulsion, is dealt with by the free solvent, the converse being the case for aluminium,

carborundum, tripoli, etc. The surface tension of the multiple phase system against oil is also claimed to be less than that of the emulsion.

It is essential that the spray should contain some unemulsified solvent, since under these conditions preferential wetting of the metal surface will occur whilst the solvent phase will dissolve oils and greases. The aqueous phase constantly washes away the solvent phase, which is in turn replaced by fresh solvent. The aqueous phase in a correctly formulated emulsion cleaner will meanwhile preferentially wet the insoluble contaminants and carry them away, whilst also removing water-soluble material.

The influence of surface active agents has also been investigated.⁽¹⁾ The fact that such a material lowers the interfacial tension between water and oil does not ensure that it will increase the tendency of the aqueous phase to displace oil from a solid surface; the interfacial tension between the solid and liquid phases must also be considered. Distilled water was found to be effective in removing a mineral oil-umber suspension from steel under controlled conditions, but neutral soap solutions would not do so in the absence of alkali. This is explained as being due to hydrolysis of the soap, fatty acids causing the latter to become attached to the metal. Approximately 0.2 per cent of oleic acid needs to be present in the oily part of the contaminating fluid to increase the adhesion markedly. The diphasic solvent cleaner used in this work consisted of mineral spirits 56; triethanolamine 2; oleic acid 4; butylcellosolve 1; pine oil 15.

Emulsion cleaners have a considerable potential field of application because of their low operating costs and efficiency. They only produce a physically clean surface, however, which is suitable for phosphate treatment, painting, or similar processes. If plating is to be carried out a chemically clean metal is needed, so that alkaline treatment is essential after emulsion cleaning and before the plating operation. Emulsion cleaning is therefore likely to find application in the plating cycle as a substitute for trichlorethylene degreasing, which likewise only effects a physical cleaning of the metal surface.

Emulsion cleaners are made up or supplied as a mixture of the solvent or solvents and the emulsifying agents, with little or no water. This may be used undiluted, but the advantages of non-inflammability are naturally not obtained if the cleaner is based on a petroleum or cheap coal-tar solvent. It is therefore usual to dilute the product by mixing with water in the proportion of $\frac{1}{3}$ to 3 per cent to form a milky emulsion. The water used must be softened to avoid breakdown of the emulsion. The operating temperature in soak tanks is 120° F. to

180° F. as the emulsion tends to break down at higher temperatures, forming a layer of solvent on the surface. With spray equipment, however, higher temperatures can be used with advantage as the emulsion is re-formed by the pumping and spraying process.

Chlorinated Hydrocarbons. In modern metal-finishing practice, practically all solvent degreasing, where it is carried out, makes use of a chlorinated hydrocarbon as the solvent medium, and it is generally employed in specially designed plant. There are a number of chlorinated hydrocarbons manufactured commercially for a variety of purposes, all of which are very powerful solvents for oils, greases, and waxes, and have the great advantage of non-inflammability. They confer their non-inflammable characteristics on other solvents when mixed with the latter, provided the proportion of the inflammable constituent is not excessive. Some of the characteristics of a few typical chlorinated hydrocarbons are shown in Table XV.

TABLE XV

Solvent	Composition	Sp. Gr.	Boiling-point °C.
Methylene dichloride .	CH_2Cl_2	1.346	42.0
Chloroform .	CHCl_3	1.50	61.2
Carbon tetrachloride. .	CCl_4	1.62	76.8
Dichlorethane .	$\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$	1.25	83.7
Tetrachlorethane .	$\text{CHCl}_2.\text{CHCl}_2$	1.601	145.0
Pentachlorethane .	$\text{CHCl}_2.\text{CCl}_3$	1.690	159.0
Trichlorethylene .	$\text{CHCl} : \text{CCl}_2$	1.47	86.7
Perchlorethylene .	$\text{CCl}_2 : \text{CCl}_2$	1.624	120.0

These solvents are to a varying extent narcotic and toxic; they are solvents for many cellulose esters, rubber, resins, etc. Carbon tetrachloride attacks copper and lead slightly; trichlorethylene, on the other hand, does not affect these metals, but iron and steel are very liable to rust after degreasing by means of the solvent. This is probably not due to any attack by the solvent on the metal itself, but because the grease-free surface makes it especially liable to be corroded by the atmosphere. On the other hand, some reaction takes place with aluminium and magnesium in the case of the hot solvent or its vapour, and when these metals are in the finely divided state, the reaction may be quite rapid, resulting in the partial decomposition of the solvent.

Trichlorethylene. On account of its extremely high solvent properties for oils and its low toxicity as compared with other compounds of this group, trichlorethylene is by far the most extensively used organic metal degreasing solvent. Its properties in many respects closely approach the ideal requirements of an organic solvent which have already been listed above.

Trichlorethylene is a clear, colourless liquid, readily volatile, and boiling at 86.7°C . Its physical properties are summarised in Table XV. The low specific heat and latent heat of vaporisation make it especially useful in hot solvent and vapour degreasing plants, since

TABLE XVI
PHYSICAL PROPERTIES OF TRICHLORETHYLENE

Composition	$\text{CHCl} : \text{CCl}_2$
Boiling-point	86.7°C .
Freezing-point	-73°C .
Specific heat	0.241
Latent heat of vaporisation	57.24 cal./gm. 1,514 B.Th.U./gal. 103 B.Th.U./lb.
Specific gravity	1.47
Gallons per ton	152
Refractive Index $\text{N}_{20\text{D}}$	1.4782
Viscosity (gm./cm./sec./ 25°C .)	0.00549
Vapour pressure at 20°C . (68°F .)	64 mm.

it is readily heated up and boiled with a small input of power. Thus the heat required to convert 1 lb. of water into steam is sufficient to vaporise $8\frac{1}{2}$ lb. of trichlorethylene. Owing to its low surface tension trichlorethylene penetrates readily into crevices and wets metal surfaces quickly. Trichlorethylene is not inflammable, neither does it form combustible or explosive mixtures with air. It dissolves most greases, oils, tars and gums very readily, and also rubber and many resins. It is not affected by water, and, in fact, the contaminated solvent is often recovered by steam distillation. The presence of water can, however, result in corrosion of metal if the solvent has undergone any degree of decomposition with the liberation of hydrochloric acid. Water dissolves in trichlorethylene to the extent of 0.025 per cent by weight at 18°C .

Trichlorethylene decomposes at temperatures in excess of 130°C ., so that local overheating of the solvent is to be avoided, whichever the means of heating that is adopted. In the case of heating by steam

coils, the pressure should not exceed 30 lb. pressure, in order to avoid such overheating.

Stabilisers.—Apart from high temperatures, trichlorethylene is affected by light, exposure to which results in slow decomposition with the liberation of hydrochloric acid. Such decomposition is undesirable, not only because of wastage and deterioration of solvent, but because the liberated acid may severely attack the metal being degreased and also the galvanised iron of which degreasing plants

TABLE XVII

RATIO OF DEGREE OF DECOMPOSITION OF TRICHLORETHYLENE WHEN EXPOSED TO ULTRA-VIOLET LIGHT AS COMPARED WITH THAT OF TRICHLOR-ETHYLENE CONTAINING VARIOUS ADDITIONS

Stabiliser (0.1 gm. per 100 c.c. solvent)	Decomposition ratio
Dibutylamine	220
Diphenylguanidine	160
Diphenylamine	132
Monoethylamine	126
Cresol	88
Diethylamine	73
Aniline	69
Triethylamine	48
<i>n</i> -Amylamine	45
Pyridine	10
Cyclo-hexanol	2
Benzol	1

are generally constructed. For this reason a good deal of investigation has been carried out on the addition of stabilisers to prevent decomposition, and all commercial trichlorethylene used for degreasing purposes contains an added stabiliser of some description. The materials used are generally basic organic compounds, e.g. amines. Table XVII shows the ratio of the degree of decomposition of pure trichlorethylene as compared with that of trichlorethylene to which 0.1 per cent of various stabilisers has been added when samples were simultaneously exposed to a mercury vapour lamp for a given period.

As the solvent builds up in oil content, it must be distilled in order to free it from contamination. The amount of oil and grease contained by the solvent at any stage can be gauged with sufficient

accuracy from a determination of its specific gravity. Table XVIII shows the specific gravity of trichlorethylene liquor at 15° C. when containing dissolved oil. This table is based on contamination by oil of specific gravity 0.926, but is approximately correct for the general types of oils removed in the degreasing of metal parts.

When it becomes heavily contaminated with oil containing soap, trichlorethylene is liable to foam, so that redistillation for the cleaning and recovery of the solvent should be carried out with care.

TABLE XVIII

TRICHLORETHYLENE CONTENT OF OIL-CONTAMINATED SOLVENT

Density: °Tw.	Specific gravity	Percentage trichlorethylene
94	1.47	100
83	1.41	90
72	1.36	80
61	1.30	70
50	1.25	60
39	1.19	50
28	1.14	40
17	1.08	30
6	1.03	20
—	0.99	10
—	0.95	5

Perchlorethylene.—This solvent is becoming increasingly used for certain applications, particularly in the United States and in Germany. For articles of light gauge, the use of perchlorethylene permits of a longer condensing and draining time being obtained because of the higher boiling-point of the solvent. On the other hand, the greater boiling-point involves the use of higher steam pressures for heating; this is offset to a small extent by the somewhat lower heat of vaporisation of perchlorethylene (90.2 B.Th.U. per lb. as compared with 103 B.Th.U. per lb. for trichlorethylene). Some properties of this solvent are given in Table XIX.

The greater density of perchlorethylene vapour is also helpful in reducing solvent losses by keeping the vapour within the plant, whilst the high boiling-point serves to eliminate water vapour from the solvent, and this reduces any tendency for hydrolysis to occur with the formation of hydrochloric acid. It has also been claimed that

perchloroethylene is less toxic than trichloroethylene, but this view is not substantiated by more recent experiments.

In general, it can be said that trichloroethylene is the most useful solvent for degreasing. In special cases perchloroethylene may be more satisfactory, however. Thus the latter solvent is more stable in the presence of aluminium, and might be worth employing where large quantities of the latter metal are being handled. Also, mercury compounds may form unstable combinations with trichloroethylene; with perchloroethylene this does not occur.

Under conditions where water-cooling coils are not able to control

TABLE XIX

PHYSICAL PROPERTIES OF PERCHLOROETHYLENE

Composition	C_2Cl_4
Boiling-point	$120.7^\circ C.$
B.P. of azeotropic mixture with water	$87.7^\circ C.$
Solvent : water ratio of azeotropic mixture	5.32 : 1
Specific heat	0.215
Latent heat of vaporisation	50.4 cal./gm.
Vapour density	5.83
Sp. gr. of liquid	1.624
Heat required to boil and vaporise solvent	73.0 cal. gm.

the level of solvent vapour satisfactorily when trichloroethylene is used, perchloroethylene proves more satisfactory. Such conditions prevail in hot climates, and also at high altitudes.

DEGREASING PLANTS

In order to obtain the maximum advantage from the grease-dissolving properties of trichloroethylene, the solvent must be used in a properly designed plant; this will also ensure that the degreasing operation is carried out with due economy and with the maximum of safety.

The three main types of plant in current use are: (a) vapour plants; (b) liquor-vapour plants; (c) multi-liquor plants. The plants themselves are generally constructed of galvanised iron, which stands up very well to the action of the trichloroethylene liquid and vapour provided decomposition of the solvent does not take place; in the latter event, rapid attack of the galvanised coating will occur. The parts to be cleaned may be lifted into and out of the plants by hoist or by hand suspended from hooks or in baskets. Various types of

mechanically operated plants have been designed in which the parts are loaded on to conveyors and pass through automatically, being discharged at the other end in the degreased condition.

Vapour Plants.—The vapour-type of plant consists essentially of a tank in which a small amount of solvent is boiled. Near the top of the tank is a bank of copper condensing coils through which cold water circulates, so that the vapour is prevented from rising to an excessively high level and overflowing the tank. The arrangement is shown diagrammatically in Fig. 36. The cooling coils do



Fig. 36.—Vapour plant, popular model, steam-heated

not, of course, prevent the conduction of heat through the walls of the plant to the region above the coils, and this results in convection currents being induced which tend to assist the carrying of trichloroethylene vapour into the atmosphere. For this reason a channel is generally welded to the exterior of the plant just above the vapour level; this reduces conduction of heat up the walls of the plant and lessens convection losses.

In operation, the metal parts to be degreased are suspended in the vapour. Since they are cold to start with, vapour condenses on to them, dissolving the oil, and running off into the sump. This process continues until the articles reach the temperature of the vapour, when no further condensation can take place. Clearly,

with articles of thin section, the condensation cleaning action will continue for a shorter time than with more massive articles, which take considerably longer to heat up.

It is to be noted that, as only pure condensate reaches the surface being cleaned, there is no possibility of contamination taking place as a result of dirty solvent residues being left on the metal surface. Also, the condensation and running off of the solvent has a mechanical

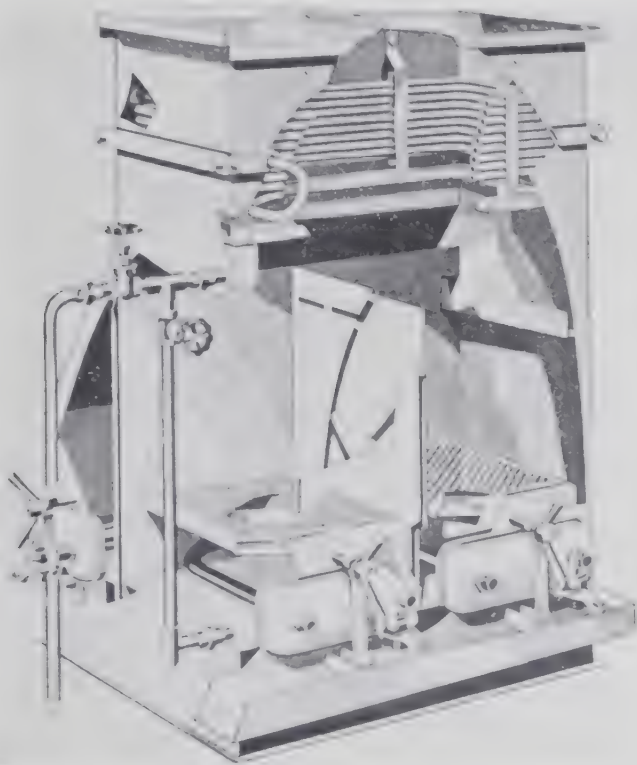


Fig. 37.—Multi-liquor (two-stage) steam-heated plant

cleaning action, so that not only is oil removed, but also, to a certain extent, abrasives, metal swarf, and soaps which may not themselves be actually soluble in the solvent.

Liquor Plants.—In the multi-liquor types of plant (Fig. 37), the bottom of the tank consists of two or more compartments, each containing boiling solvent. The articles to be cleaned are immersed successively in the various sections, the cleanest solvent being in the last compartment. This is achieved by arranging for the condensate from the cooling coils at the top of the tank to be delivered into the final compartment. This type of unit is, however, less in demand

than the simpler vapour or liquor-vapour types in which most work can be satisfactorily degreased.

Liquor-Vapour Plants. Broadly speaking, vapour degreasing adequately removes oils and greases, even when these contain slight non-soluble contamination, but when such insoluble contamination is present to any considerable extent, liquor-vapour plants are to be preferred. Thus, articles which have been polished and retain a certain amount of polishing composition in recesses have to be immersed in the boiling solvent to remove the abrasive and soap residues. As the grease dissolves, the other materials are released and are washed out by the movement of the boiling solvent.

Liquor-vapour plants are also desirable where material of thin section is being treated. Such work heats up very quickly, so that vapour degreasing is not really effective unless a second immersion is given, the parts being allowed to cool off in between. This is a laborious method, and it is therefore better to treat such parts in a liquor-vapour plant.

Care should be taken in lifting parts out of the degreasing plant to see that this is carried out slowly and uniformly to prevent drag-out of vapour and of liquid in cupped parts. Various types of racks and baskets have been designed to handle such articles so as to effect rapid degreasing with a minimum of solvent loss. Fig. 38 shows a special type of basket designed for small parts, which can be rotated while in the tank by means of a ratchet and cable attachment operated from outside the plant itself. A basket of this type reduces the trapping of solvent by cup-shaped articles to an absolute minimum.

In operating the liquor-vapour type of plant, two methods are available, viz.: (1) where the work is greasy and free from solids such as polishing abrasive, it is desirable to remove the bulk of the grease by vapour treatment and follow this by a rinse in the liquor compartment; in this way the liquor compartment has but little grease or dirt added to it, and the solvent therefore is kept very clean by the automatic flow into it of condensate from the cooling coil; (2) where the work is covered with polishing dirt, it is essential that the solid particles should be washed away as fast as they are released by the dissolving of the grease-bond; therefore, the work is washed directly in the liquor compartment and raised out of it steadily to avoid excessive drag-out. The purpose of the vapour compartment in this case is to receive the dirty solvent displaced from the liquor compartment by the continuous flow of clean distillate into it. The successful action of the plant in this case depends on keeping the dirty liquor in the vapour compartment boiling freely

so as to produce the maximum amount of condensate to provide automatic self-cleaning of the solvent in the liquor compartment.

Heating.—The heating of degreasing plants can be carried out by gas, steam, electricity, high-pressure hot water, or oil. *Gas-burners* are located below the plant, and should give a uniform degree of heating over the whole bottom. A good flue must be



Fig. 38.—Ratchet and cable-operated rotating basket for degreasing small parts in manually operated plants

fitted to remove the products of combustion. In the case of gas-heated plants a remote control valve is connected to two thermostats, one being located at the top of the cooling coil, where its action is to cut off the gas supply to the main burner if the flow of cooling water is restricted so that the vapour level might rise unduly high. The second thermostat is in the sump, and cuts off the gas supply to prevent a temperature of 130° C. being exceeded in the liquor when distillation is nearing completion. Heating the solvent to temperatures above this figure may lead to decomposition and the

formation of acid, which will attack the plant. If the temperature should become very high indeed, as, for example, when the solvent comes into contact with an open flame or red-hot surfaces, breakdown of the compound takes place with the formation of phosgene and hydrochloric acid. Exposure of the solvent to such conditions must therefore be scrupulously avoided.

Steam heating is especially suitable for use with degreasers. The steam pressure should not exceed 30 lb./sq. in. with clear trichloroethylene in the plant. A safety device is fitted to steam-heated plants to shut off the steam if the water supply to the cooling coils fails or becomes inadequate.

High-pressure hot water can also be employed for heating; it is difficult to arrange for the thermostatic control of hot-water heated plants, and for this reason an orifice plate is necessary in the hot-water system, to regulate the rate of heat transfer by restricting the flow of hot water. The size of the orifice must be determined by trial, and it is also desirable to fit a warning light and a bell operating in conjunction with thermostats to notify the operator if either the sump temperature becomes too high or if the vapour level overflows the cooling coils due to failure of the water supply.

Electrical heating is readily carried out by means of thermostatically controlled heaters, fitted below the sump to avoid local overheating. This is a flexible method of heating, although it is inclined to be relatively costly.

Table XX shows the operating characteristics of five typical standard manually operated plants. The figures quoted for output and solvent consumption are only approximate, but are representative of those that can be obtained in the degreasing of heavy metal components.

Automatic Plants.—Automatic plants for degreasing are coming into extended use; these have already been referred to, and a typical installation is illustrated in Fig. 39. They have the advantages of low labour costs, the avoidance of high solvent losses due to bad handling of the work into and out of the plant, and the elimination of practically all health hazard to the operator. More often than not, however, they have to be specifically designed for the work to be degreased, which makes them more costly and perhaps rather less flexible should there be a major change in the type of parts being handled. This does not apply to such an extent to the manually operated plants, a large range of which are now available made to standardised designs and dimensions. It is impossible here to list or describe the great number of automatic degreasing installations

TABLE XX

DIMENSIONS AND OPERATING CHARACTERISTICS OF STANDARD SOLVENT DEGREASING PLANTS

Type of plant	Effective size of compartments	Overall size of plant * (approx.)			Solvent charge (galls.)	Fuel consumption (max.)	Cooling water galls. hr.	Time to start from cold		Maximum output lb. hr. approx.	Solvent consumption, cwt. degraded per gall. (approx.)
								(mins. approx.)			
								Gas	Steam		
Length Breadth Depth											
in. in. in. ft. in.											

* On steam-heated plants the safety device (measuring 2 ft. 6 in. by 10 in. by 1 ft. 9 in.), is not included in these dimensions.
 † Figures are based on an average calorific value of 500 B.Th.U. per cub. ft.

that have been constructed, and we shall have to confine ourselves to a brief description of two of the latest of this type.

The first is shown diagrammatically in Fig. 40. This was specially designed to degrease pressings in the form of shallow trays $18\frac{1}{2}$ in. by 13 in. by $3\frac{1}{2}$ in. deep which tend to cup solvent. Two of the pressings are pushed side by side, with the open side upwards, into the carrier. The carriers are shallow baskets, having an opening along the front; these are rigidly attached to the conveyor chains. As the carriers pass round the lower sprockets they become inverted,

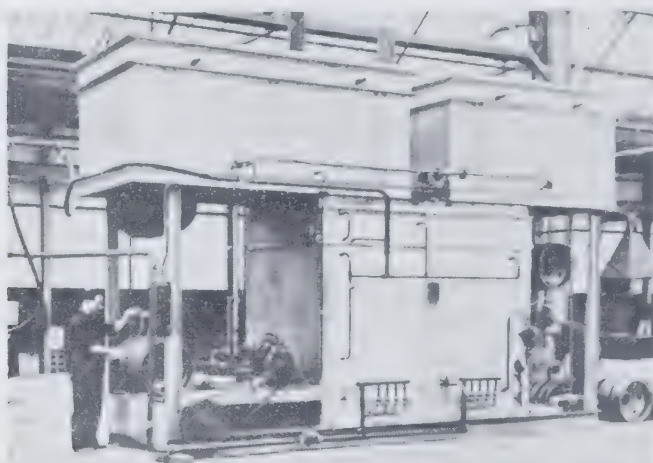


Fig. 39.—Automatic degreasing plant

but the pressings are retained in them below the sprocket centres by fixed skid bars located close up to the travel of the outer edges of their openings. The work can be unloaded at the opposite side of the plant to that at which it was loaded; it is then in an upside-down position. The conveyor speed of this plant is 3 ft. per minute, giving an output of 600 trays per hour. Of the general design it may be said that it is suitable for any class of shallow pressing which has to be inverted to release trapped solvent.

Another mechanised plant designed to degrease parts in boiling solvent liquor is shown in Fig. 41. The conveyor consists of a single chain to which are attached a series of compartmented carriers suitable for holding deep-drawn hollow articles which, in this instance, are of the order of 1 in. diameter by 3 in. deep.

The drawn parts are placed mouth downwards in the carriers; the latter pass up over a sprocket and then take the work, mouth upwards, down into the boiling liquor. Here the chain again passes round a

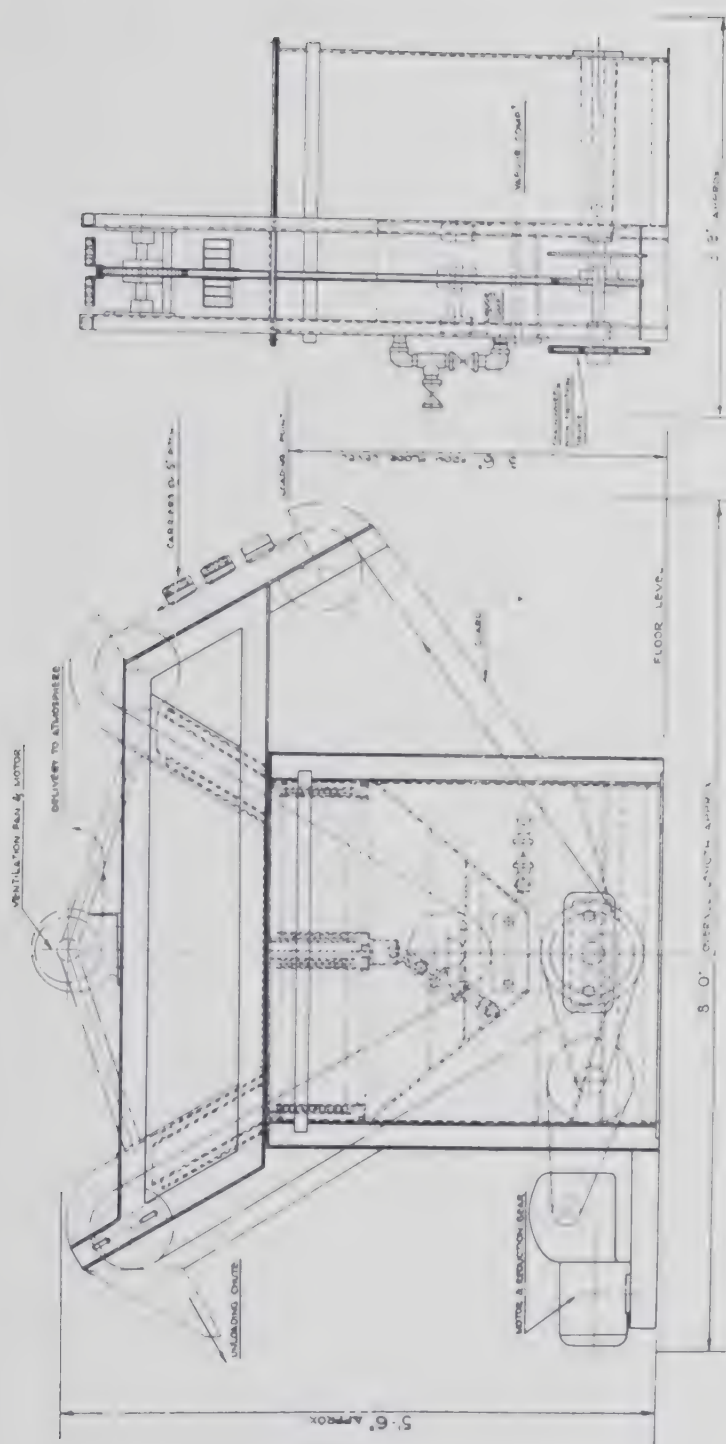


Fig. 40.—Arrangement of automatic degreasing plant for shallow pressings

sprocket, and, rising upwards, inverts the components so that the liquor drains out freely. After travelling through the cooling turret, the conveyor chain passes over another sprocket on its return path under the plant to the starting-point. It is important to note that at this last sprocket the work no longer rests against the back of its carrier, but is tilted towards the open front, whence it falls into baskets, or on to a conveyor belt.

To prevent the liquor in which the parts are washed from becoming unduly charged with grease, a concentrator forms part of the plant. The greasy liquor overflows into this as it is displaced by clean condensate from the cooling coil. Another measure to maintain the cleanliness of the liquor consists in the provision of a baffle-plate which diverts into the concentrator the bulk of the grease which is dissolved as soon as the work enters the vapour. With a conveyor speed of 4 ft. per minute, there is a possible output of 5,000 articles per hour.

Solvent Economy.—In order to obtain the maximum economy in solvent consumption, and to ensure that the best results are obtained, solvent degreasing plants need to be operated correctly. In the open-topped plant of the hand-operated type, work should be lifted from the plant slowly and steadily in such a way as to avoid disturbance of the vapour surface as far as possible. The speed of the lift in the drying-off zone of the plant should be of the order of 5 ft. per minute.⁽²⁾ In the case of conveyerised plants, the conveyor passes into and out of hooded turrets at the ends of the totally enclosed plants, which substantially prevent solvent loss. In such plants, the conveyor speed can be up to about 10 ft. per minute.

Lids are fitted to open-topped plants, and these should be kept closed as far as possible during idle periods. The roller or sliding types of lid are to be preferred, since they result in less draught and disturbance of the vapour-air interface when the lids are opened or closed. In practice, of course, there is a constant diffusion between the air and the vapour phases, and the use of the lids results in a considerable reduction in the rate at which such diffusion can take place. Gas-heated plants are especially liable to solvent losses by diffusion, due to the convection currents brought about by the gas flames and the heat from the flue-pipe.

Solvent degreasing plants should be located where there is a minimum of draught, but in cases where high solvent losses exist for one reason or another, it sometimes pays to install a solvent recovery unit. This consists essentially of a narrow duct placed round the top of the plant through which a low-power fan draws a stream

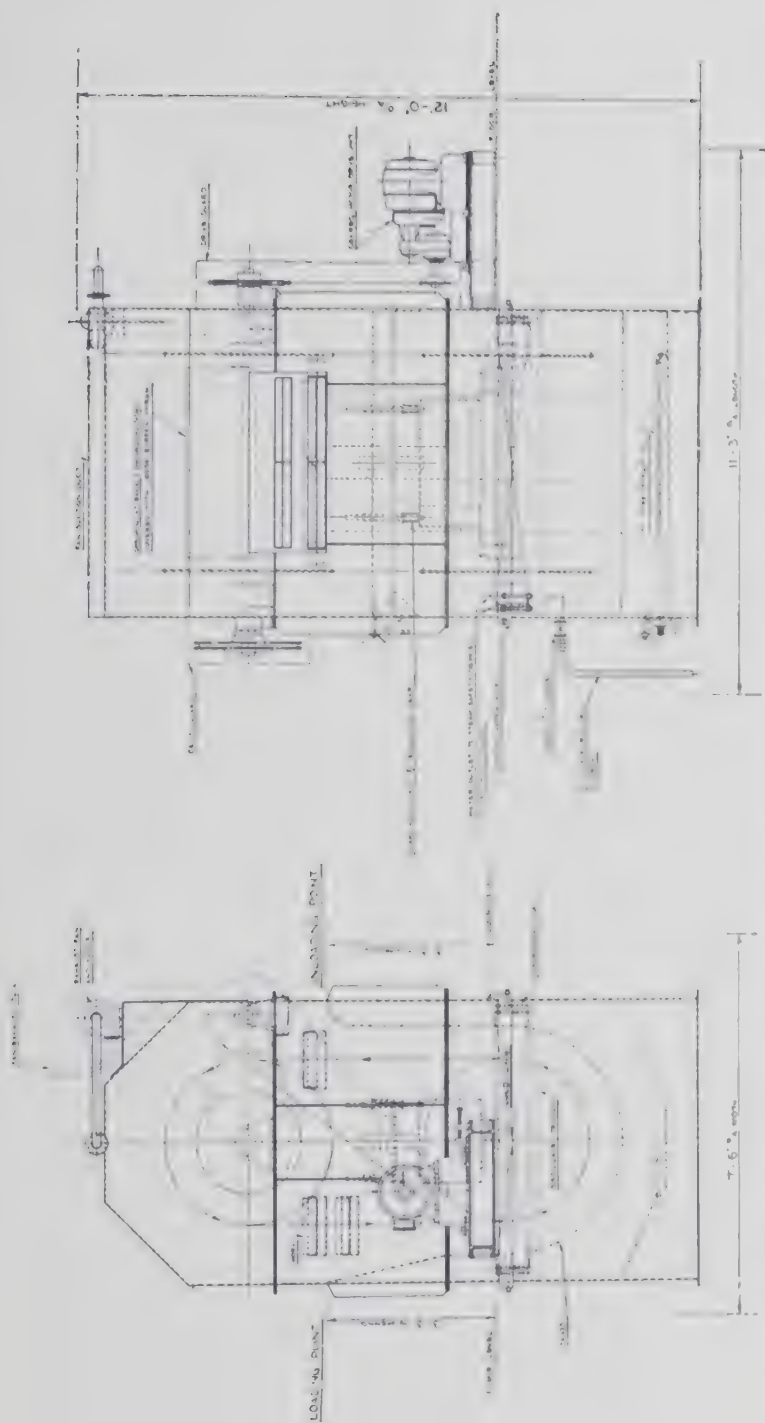


Fig. 4. Arrangement of automatic plant for degreasing small cup-shaped pressings in boiling trichlorethylene.

of air. The solvent-laden air extracted in this way is passed through a container filled with activated charcoal, which absorbs practically all the trichlorethylene carried off from the plant. This can then be recovered by periodic steam distillation of the solvent-impregnated charcoal.

Pressings and cup- or thimble-shaped articles generally result in the withdrawal of considerable amounts of solvent from the plant. In handling such articles, they should be placed in baskets lying horizontally, with the open ends facing in one direction. The baskets can be lowered into the plant with the open ends tilted slightly upwards so that air will not be trapped within them; when they are removed they are then tilted in the opposite direction so that both solvent and vapour will run out as the parts are removed. It is desirable to have some kind of a rack which is placed just above the vapour level on which the basket can be rested before withdrawal from the plant, in order that the bulk of the solvent may have an opportunity to condense. This tilting operation can be carried out mechanically in the case of hoist-operated plants carrying heavy loads.

If such a drying-rack cannot be fitted due to lack of room in the plant itself, it is useful to have a water-cooled tank closely fitting the basket and located conveniently near the plant in which the baskets can be left for a few minutes. The solvent condenses in this tank, from the bottom of which the condensate can be collected at the end of each day. A special rotating basket for use with small cup-shaped articles which enables the handling of these to be simplified considerably has already been described. (See p. 120.)

Distillation.—When a considerable amount of oil and dirt has accumulated in the solvent, the latter must be distilled off. As grease builds up in the solvent, the rate of production of vapour decreases, while the boiling-point of the liquor rises. (See p. 125.) Both these effects are undesirable, an excessive boiling temperature particularly leading to solvent decomposition. Thus, a liquor composed of a 50:50 mixture of trichlorethylene and oil distilled at a rate of approximately 73 per cent of that of clean solvent in a gas-heated plant; in a steam-heated unit this rate was reduced to only 23 per cent under the same conditions, while the presence of 35 per cent of oil reduced the rate of vaporisation of solvent by 50 per cent. A liquor composed of 20 per cent trichlorethylene and 80 per cent grease boils at about 130°C., and this temperature cannot safely be exceeded; it is, however, very desirable to clean the plant well before this stage is reached.

Special facilities are provided in all plants for carrying this out,

the condensed solvent being collected in a suitable vessel placed below the distillate pipe leading from the plant. Distillation is continued until the sump temperature reaches 130°C ., when the sump thermostat automatically comes into operation and no more solvent will distil. At this stage the plant is allowed to cool, and the residues are removed from the sump through the mud-doors by means of a rake. Distillation should not be carried on if the level drops below the steam coils. In this case the oily residue is run off and added to the contaminated liquor when the next occasion for distillation arises.

Frequent cleaning is desirable to avoid decomposition of the solvent which can be brought about not only by local overheating, but by the presence of such materials as light alloy swarf. The fact that the solvent has become acid is generally shown by the presence of a haze of hydrochloric acid over the tank, together with an acid odour, and later by the formation of green corrosion products on the copper condensing coils and corrosion of the tank walls. If the solvent becomes acid, the plant must be stopped at once and carefully cleaned out, the solvent being redistilled before use.

Aqueous Distillation.—In the best current practice, especially where there are a number of plants in operation, all plant residues are distilled in a separate distillation unit, which can be an ordinary vapour plant assigned for this purpose. The best method is to use live steam if available or the process of wet distillation whereby water is added to the oily liquor so that, in effect, steam distillation takes place. There is no risk of overheating the solvent towards the end of the distillation process as is the case when heavily oil-contaminated solvent is being distilled alone.

The addition of water to clean trichlorethylene results in the formation of an azeotropic mixture boiling at 73°C . (instead of 87°C ., the boiling-point of the pure solvent), so that practically all the solvent can be recovered by the use of temperatures little exceeding 100°C . The amount of water required is not critical, about 2 gallons being sufficient for the most commonly used plant sizes.

It is necessary, however, to fit a water separator when aqueous distillation is employed. This prevents water being carried into the drum into which the distillate flows, while it also allows the stabiliser to be retained in the trichlorethylene if the water flowing from the separator is constantly returned to the greasy liquor, until complete recovery of the solvent has been effected.

A further advantage of this method is that the time for cleaning a plant is much reduced, it being only necessary to drain or pump

the dirty solvent out before sending it to the still. Meanwhile, the plant can be immediately filled with a fresh charge of solvent and is ready for use again.

FRASER-HELLER PLANTS

The "Fraser-Heller" Degreasing Plants are claimed to save a very considerable proportion of the trichlorethylene used in the type of plant already described.

The essential feature of the degreasing tank is a condenser of water-cooled gilled tubes made in two halves and covering its cross-section. The condenser halves can be swung to the sides of the plant by means of a lever for the lowering and raising of the basket which holds the articles to be degreased. After the basket has passed the condenser, the latter is raised into the horizontal closed position for the degreasing action to take place. The plants are made for use with either static or rotating work-baskets.

Before starting operations, the trichlorethylene in the sump of the tank is brought to the boil by steam, gas or electricity, so that the vapour condenses upon the water-cooled gilled tubes, the lowest point of each fin of which constitutes a predetermined drip-point. A continuous, dense and equally distributed rain of pure, hot trichlorethylene thus pours down from the condenser. Normally, the work-basket is first put into the lower compartment where it is rotated under the rain of solvent from the condensers. Insoluble matter, on being rinsed down, is retained on the filter trays placed between the basket and the sump to prevent it from being deposited on the heating surfaces. The basket is then lifted into the upper compartment and again rotated at very low speed to drain the trichlorethylene from hollow articles, whilst at the same time the parts are dried. Rotation is then stopped for about a minute so that the dense trichlorethylene vapour may condense into the sump.

The essential feature of the plant is that the liquid solvent is always pure and uncontaminated, whilst the duration of the solvent washing process is independent of the thermal capacity of the articles being treated. Thus articles of light gauge can be subjected to the action of the vapour for a longer period than is possible with a vapour degreaser of the conventional type.

The condenser also closes the lower compartment from the upper one, thus retaining the heavy vapours in the former, and reducing solvent losses from the open top of the plant. The condenser, when required, can also be used periodically as a distilling unit for solvent purification. By means of a pair of guiding plates underneath the

condenser, the redistilled trichlorethylene can be led into gullies, whence it is piped out of the plant into suitable containers.

As a further refinement where high solvent losses may be encountered a recovery plant can be added. In this case a fan is arranged to extract the air from the degreasing chamber before it is opened and pass it over activated carbon where the trichlorethylene is absorbed, any surplus being held in the condenser. The solvent

1. Degreasing tank
2. Cover
3. Condenser opening gear
4. Condenser
5. Perforated basket
6. Dirt trap
7. Guttering
8. Suspension chains
9. Sump

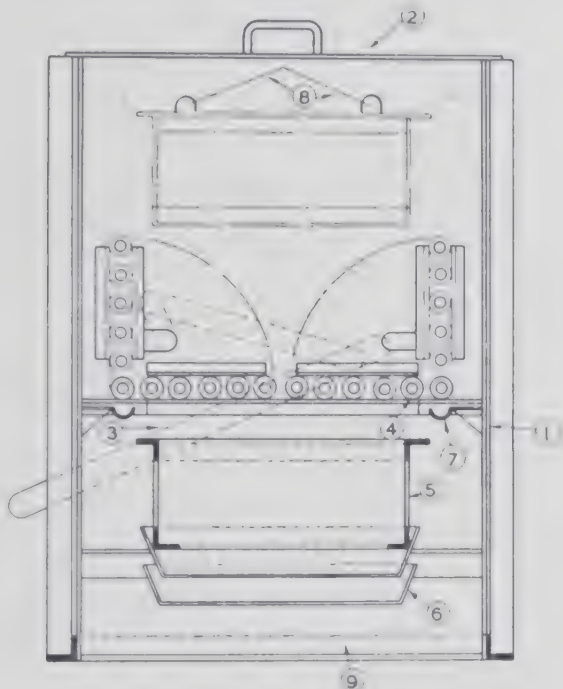


Fig. 42.—Fraser-Heller degreasing chamber

can then be recovered periodically by steam distillation and separation in the condenser.

The general arrangement of the Fraser-Heller degreasing unit is shown in Fig. 42.

It will thus be seen that the plant operates in a definite cycle, and trichlorethylene losses are negligible. Owing to the somewhat elaborate nature of the plant it is costly to install and is therefore only worthy of consideration where trichlorethylene consumption is high.

Trichlorethylene degreasing is a very effective method of removing oily and greasy contamination from metals, as is shown by its present widely extended use in industry. It must, however, be borne in mind that it does not constitute a complete cleaning process in itself where a chemically clean surface is required, as, for example, when

metals are to be electro-plated. In such cases, degreasing must be considered as a preliminary operation, the final cleaning being generally carried out in solutions of alkalis.

ALKALINE CLEANERS

Alkaline cleaning methods are used either alone, for removing surface contamination of an oily nature from metals, or following on solvent degreasing to produce a chemically clean surface, suitable for subsequent finishing operations. The alkalis which are employed in present-day practice are relatively limited in number; each has its own specific characteristics, however, and, as a rule, a combination of several alkalis is used in the formulation of a cleaner. In addition, small quantities of soaps may be added to facilitate wetting and deflocculation or peptisation of colloidal surface contaminants, whilst synthetic wetting agents are also useful in lowering the surface tension of alkali solutions which may tend to be on the high side.

Saponification as a characteristic of a cleaning solution has already been referred to; the process consists essentially in the formation of water-soluble soaps by the interaction of the alkali present with the oil or grease, which it is desired to remove. Mineral oils are not capable of being saponified in this way by alkalis to any appreciable extent, so that other phenomena must be brought into play if effective cleaning action is to be obtained when these are present in quantity. Chief amongst these is emulsification. By this is meant the suspension of the oil in the form of fine droplets (which may be of the order of 10^{-5} mm. in diameter, or less) in the water medium.

Emulsification.—The efficiency of a detergent as an emulsifying agent is determined by its ability to promote the spontaneous dispersion of the oil in the form of fine droplets, coupled with its ability to prevent their re-coalescence. Emulsifying agents are characterised by their tendency to concentrate in the interface between the oil and the water. Their molecular structures, therefore, consist usually of a long chain hydrocarbon portion, which has an affinity for the oil portion of the dispersion, attached to a polar or water-soluble atom or group, e.g. a sodium atom, sulphonic acid derivative, etc. This type of structure is typical of the soaps and the synthetic wetting agents, which will be examined in greater detail below.

It has generally been assumed that emulsification of an oil takes place by penetration of the detergent solution through the oil layer by virtue of its low surface tension with wetting of the underlying metal. The effect of the solution would therefore be to split up the oil into a multitude of droplets which would thereupon be separated

from the basis metal. Recent work has, however, shown that on immersion in a detergent solution the oil film contracts rather than increases its surface area.⁽³⁾ In so doing, it forms globules which are readily separated from the metal surface by the alkaline solution. This indicates that the wetting of the metal by the alkaline solution is of greater importance than the wetting of the oil layer.

The emulsifying agents are also always, to a degree, wetting agents, and it is difficult to distinguish clearly between these phenomena.

Deflocculation.—Besides emulsification, deflocculation will take place as a result of detergent action. By deflocculation is meant the disintegration of the contaminant prior to its emulsification and suspension in the aqueous phase. In this sense deflocculation is the opposite to agglomeration. The deflocculating agent acts by separating the particles so that the residual forces tending to hold them together, or to cause flocculation, are prevented from acting; its effect may consist in its being adsorbed on the surfaces of the oily particles preventing the formation of stable agglomerates. When a dirty metal surface is immersed in an alkaline solution the first process which takes place is probably the saponification by the alkali of any proportion of saponifiable material which may be present. This is followed by a wetting action, in which the detergent concentrates at the interface between the contaminant and the detergent solution so that deflocculation and emulsification of the foreign materials present are brought about.

The material removed must be suspended in the cleaning solution in such a way that rinsing will leave a clean metal surface. An unstable dispersion is unsatisfactory, as it may lead to the reprecipitation of the grease on the metal. The stability of the dispersion depends on the adsorption of the detergent at the oil-water interface, but micelles carrying similar electrical charges may facilitate stabilisation. For this reason, the addition of very small quantities of colloidal material to a detergent may often give a very marked improvement in its cleaning properties.

The ability of a particular solution to clean a metal surface is thus a combination of a considerable number of factors, including the lowering of the interfacial tension between the water and the oily phases, the dispersing and deflocculating powers of the solution and foaming properties which promote suspension.

It is of interest to note that scouring and mechanical action may in some cases actually give inferior cleaning.⁽⁴⁾ This can probably be ascribed to the breakdown of the emulsion of the oil in the cleaner, as a result of the oil particles being forcibly brought into close contact

with one another, breaking down the protective surface film. Re-precipitation of the oil on the metal surface then takes place.

It is sometimes an advantage where a great deal of grease has to be removed to have two cleaners. The first is used as a soaking bath and the alkali employed here is not one with specially good emulsifying properties. The grease is removed and floats to the surface, whence it can be skimmed off. Thus, the bulk of the solution does not become heavily contaminated with emulsified oil. The partly cleaned work is then transferred to the second cleaner, which should have good emulsifying and peptising properties.

Alkalis Employed.—*Caustic soda*, NaOH , is one of the most useful of alkaline cleaning agents. Its solutions have the highest pH value and saponifying properties of any of the alkalis, although its emulsifying properties, so far as solid dirt or mineral oils are concerned, are not very good. Not only does its high solubility enable strongly alkaline solutions to be produced, but, unlike sodium carbonate, its use will not result in the formation of insoluble compounds. Owing to its causticity, it is, however, more difficult to handle and to use than sodium carbonate, whilst it is considerably more expensive than the latter alkali. Caustic soda is produced electrolytically, and is available in the fused or the flake form. The latter is to be preferred for ease of handling in the making up of cleaning solutions. The commercial material may contain up to 2 per cent of sodium chloride.

One disadvantage of caustic soda is that it is most difficult to rinse from metal surfaces. Residues may dry and form carbonates or react with the metal. A substantial improvement can be effected by the incorporation of a small amount of *sodium hexameta-phosphate* in the solution. As little as 0.001 per cent will have a marked effect in improving rinsability characteristics.

Caustic potash, KOH , has found favour as an alkaline cleaner in electro-plating practice in preference to caustic soda to some extent because of its higher electrical conductivity, despite the fact that it is considerably more expensive. The commercial product contains about 90 per cent KOH .

Sodium carbonate is the cheapest and most readily available alkali suitable for use as an alkaline cleaner ingredient. The anhydrous salt, Na_2CO_3 , is known in the trade as *soda ash*. This is the most economical form in which it can be purchased. The decahydrate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, washing soda, is efflorescent, and contains a high proportion of water. Soda ash is, however, rather slow in dissolving, and for this reason the monohydrate, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, produced by

crystallising the solution at temperatures above 35°C ., has found some favour. This material is stable, is readily dissolved, and has only a low water content. It is still, however, relatively expensive, and for this reason its application is very limited. Sodium carbonate solutions wet some kinds of contaminants more readily than do caustic soda solutions, whilst they also tend to rinse away more readily than caustic soda-containing solutions which tend to adhere very strongly to metal surfaces.

Mixtures of caustic soda and sodium carbonate are known as *causticised ash*, and these are available for detergent purposes, whilst a double salt, sodium sesquicarbonate, $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$, is also marketed.

Sodium silicates are useful detergents, and the term includes materials ranging from "water-glass", a viscous liquid, to granular sodium metasilicate, in various states of hydration. The compositions of the silicates as supplied vary considerably, and they do not always correspond to the requirements of a precise chemical formula. Broadly speaking, so far as metal cleaning requirements are concerned, the important factor is the $\text{Na}_2\text{O} : \text{SiO}_2$ ratio of the material. Wernick⁽⁵⁾ recommends sodium silicate having a content of 9.5 per cent Na_2O and 30.5 per cent SiO_2 as the most economical material to use. Sodium metasilicates are obtainable having the compositions $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ and $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ approximately and in other degrees of hydration. The silicates are useful in the cleaning of metals readily attacked by alkalis, as they have an inhibiting effect on the action of the more aggressive alkalis on these metals. Sodium silicate rinses fairly freely and is a good peptising agent. Its emulsifying properties are also good and its presence does not unduly depress the emulsifying characteristics of soap-containing solutions. The metasilicate is preferable if any considerable proportion of saponifiable oils is likely to be present.

Trisodium phosphate is widely employed in metal cleaning on account of its free-rinsing properties and the fact that its action on metals, such as zinc and aluminium, is small. It is, however, a relatively mild detergent, and its peptising action is not as good as that of sodium metasilicate. Trisodium phosphate is commercially available as a free-flowing material in the form of needle-shaped crystals consisting substantially of the dodecahydrate, $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$. It is readily soluble in water, the solubility increasing rapidly with temperature. Thus a saturated solution at 20°C . contains approximately 10 per cent by weight of Na_3PO_4 , whilst at 100°C . it contains 45 per cent. A solution of 0.2 per cent by weight of the crystalline

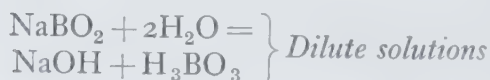
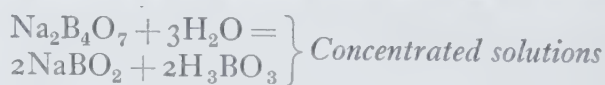
salt has a pH of 11.7 at 20° C. The crystals contain impurities in the form of sodium hydroxide and sodium carbonate, but these constituents do not exceed 2.5 per cent.

The anhydrous tribasic phosphate is also marketed as a white powder.

Tetrasodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7$, finds rather more limited application in cleaning. It is less soluble than the tribasic phosphate, but the solution is very stable and hydration to the orthophosphate only takes place very slowly. A 1 per cent solution has a pH of 10.2, equivalent to that of a neutral soap. It is an effective water-softener, and its use in combination with soda ash and metasilicate has been recommended for the cleaning of aluminium.

A number of other phosphates have also been developed for use in cleaning mixtures.

Borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, is sometimes used as a very mild alkali in cleaners; the solution undergoes hydrolysis with the formation of boric acid, which is a very weak acid, leaving the solution alkaline.



Soaps, such as rosin soap or sodium oleate, are commonly used as ingredients of cleaners in small amount, to decrease the surface tension of the solutions and promote wetting and peptisation. The soaps generally, and particularly rosin soaps, suffer from the disadvantage of having relatively low solubility in cold water, and so are liable to leave deposits on articles on rinsing. This solubility is decreased still further if any considerable proportion of caustic soda is present in the cleaner. This is quite apart from the well-known fact that soaps are precipitated by hard water. The limitations of soaps will be examined in greater detail when surface tension and wetting agents are discussed below.

Sodium aluminate is also sometimes found in proprietary cleaner mixtures, as, like sodium silicate, it reduces the attack of alkalis on metals such as zinc and aluminium. These materials are prone to leave films on the latter metals, however, which are somewhat difficult to rinse away. On occasion, solid insoluble constituents, such as china clay, are employed, which act by absorbing liberated dirt, but such materials tend to settle out and their use is not to be advocated.

Cyanides are also employed to some extent because of their ability

to remove tarnish films from polished metals, such as brass, but it is probably preferable to omit cyanides from cleaner formulae and to use a weak solution of sodium cyanide as a dip after cleaning has been carried out, particularly on copper alloys. This will have the effect of removing any tarnishing which may occur in cleaning.

Balance of Cleaner Compositions.—Cleaner compositions must be carefully balanced, so that the optimum cleaning efficiency is obtained with the least destructive action on the metal. Some metals (e.g. zinc and light alloys) are very readily attacked by caustic

TABLE XXI

RATE OF DISSOLUTION OF TIN AND ALUMINIUM IN ALKALINE SOLUTIONS

Alkali	Tin (180° F. for 1 hr.)			Aluminium (212° F. for 1 hr.)		
	Concn. oz./gal.	pH	Wt. loss: gm./sq. in.	Concn. oz./gal.	pH	Wt. loss: gm./sq. metre
Soda ash, Na_2CO_3	0.4	11.2	0.79	1.6	11.4	31.60
T.S.P. $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	0.4	11.6	0.92	1.6	12.0	21.90
Sodium metasilicate, $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$	0.4	12.0	0.14	1.6	12.6	0.22
Sodium sesquicarbonate: $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$	0.4	10.0	0.47	—	—	—
Caustic soda, NaOH	—	—	—	1.6	13.5	129.0

alkalis. The pH of the alkaline solutions used in dealing with these metals must be controlled (p. 149). Trisodium phosphate is especially applicable to the cleaning of zinc-base alloys, whilst sodium silicate has a strongly inhibiting action in preventing attack on such metals.

Cleveland⁽⁶⁾ gives comparisons of the rate of dissolution of tin and aluminium in various alkaline solutions (Table XXI). The low solubility of the metals in sodium metasilicate solutions is noteworthy.

Mabb⁽⁷⁾ quotes the analysis of a number of proprietary alkaline cleaners and these are shown in Table XXII.

The makers recommend the use of these materials in concentrations of 2 to 5 per cent, the solutions being employed at temperatures of from about 50°C. to boiling-point.

Active Alkali.—The activity of a cleaner may be measured by its active Na_2O content, this being defined as the amount of Na_2O

TABLE XXII

ANALYSIS OF SOME TYPICAL PROPRIETARY CLEANERS (MADE)

Composition per cent.	1 (Small lumps)	2 (Pow- der)	3 (Pow- der)	4 (Pow- der)	5 (Pow- der)	6 (Moist jelly)	7 (Pow- der)
Caustic soda, NaOH .	—	—	—	41.9	—	23.6	20.2
Sodium carbonate Na ₂ CO ₃	—	—	—	55.5	41.0	—	—
Sodium silicate .	58.7	54.1	—	—	26.1	8.5	31.7
Trisodium phosphate .	—	—	52.9	0.8	7.5	—	6.9
Glycerin	—	—	—	—	—	13.0	—
Sodium oleate . . .	—	5.3	—	—	—	—	11.2
Water	41.3	40.6	47.1	1.8	25.4	54.9	30.0

available at a pH in excess of 8.3, it being generally recognised that alkaline solutions exert little cleaning action at a pH of less than this. The total Na₂O content is determined by titration with acid, using methyl orange as an indicator; the active Na₂O is found by titration in the presence of phenolphthalein, which changes colour at the appropriate pH value. The active and total Na₂O contents of some of the commoner alkalis are given in Table XXIII.

TABLE XXIII

ACTIVE AND TOTAL Na₂O CONTENTS OF SOME ALKALIS

Alkali	Active Na ₂ O	Total Na ₂ O
Caustic soda (NaOH)	75.5	76.0
NaOH-sod. metasilicate mixture (50 : 50)	51.5	52.6
Sodium metasilicate (Na ₂ SiO ₃ ·5H ₂ O)	28.0	29.2
Trisodium phosphate (Na ₃ PO ₄ ·12H ₂ O)	10.0	18.0
Sodium carbonate (Na ₂ CO ₃)	29.0	58.0
Tetrasodium pyrophosphate (Na ₄ P ₂ O ₇)	8.1	23.3
Borax (Na ₂ B ₄ O ₇ ·10H ₂ O)	8.4	16.3

pH Values.—The pH value of the solution is often accepted as a partial measure of the effectiveness of a cleaner. The pH value is also a useful guide in estimating the relative conductivities of alkalis, since the electrical conductivity of an electro-alkaline cleaner is an important factor in its efficiency. The pH values of solutions of different concentrations of a number of alkalis are shown in Table XXIV.

TABLE XXIV

pH VALUES OF VARIOUS CONCENTRATIONS OF REPRESENTATIVE ALKALIS
AT 20°C.

Alkali	Concentration						
	0.01 per cent	0.05 per cent	1 per cent	0.15 per cent	1 per cent	5 per cent	10 per cent
NaOH	11.6	12.1	12.6	13.0	13.5	14.0	14.0
Na ₂ CO ₃	10.4	10.7	11.0	11.2	11.4	11.5	11.6
Na ₂ SiO ₃ .5H ₂ O	10.6	11.2	11.6	12.1	12.5	12.9	13.4
Na ₃ PO ₄ .12H ₂ O	10.5	10.9	11.3	11.6	12.0	12.3	12.6
Na ₂ CO ₃ .NaHCO ₃ . 2H ₂ O	10.2	10.1	10.1	10.0	9.9	9.7	9.4
Na ₂ B ₄ O ₇ .10H ₂ O	9.1	9.1	9.1	9.2	9.2	9.3	9.4

The pH value of a cleaner should be about 9 to 10 for the softer metals, such as zinc, aluminium, and tin-lead alloys, increasing to about pH 10 to 11.5 where light grease has to be removed. For heavier contamination, pH values in excess of this may be found necessary. The general run of cleaners used in the electro-plating trade have pH values of between 11.5 and 13 for copper, brass, and steel, but where substantial deposits have to be removed, cleaners of pH as high as 13 to 14 are often employed.

The pH value is determined either by means of a suitable electro-metric apparatus, or more simply by the use of chemical indicators which undergo colour changes within the pH range concerned. The colour changes of some of the indicators which prove useful in the measurement of the pH of alkaline solutions are given in Table XXV.

TABLE XXV

COLOUR CHANGES OF ALKALINE pH INDICATORS

Indicator	Colour change	pH range
Thymol blue	Yellow to blue	8.0-9.6
O-Cresolphthalein	Colourless to purple	8.2-9.8
Phenolphthalein	Colourless to red	8.3-10.0
Thymolphthalein	Colourless to blue	9.3-10.5
Alizarin yellow G	Yellow to orange	10.1-12.1
Brilliant cresyl blue	Blue to yellow	12.0-12.4
Tropæolin O	Yellow to orange	11.1-12.7

Surface Tension. An important point in connection with soaps and alkaline solutions is that the surface tension of such solutions decreases as the pH rises. The surface tensions of solutions of sodium oleate at different pH values have been determined by Powney and Addison⁽⁸⁾ and are shown in Fig. 43. The oil globules in suspension are themselves electrically charged, and this charge facilitates the formation of a stable emulsion, owing to the mutual electrostatic repulsion of the globules, preventing the re-precipitation

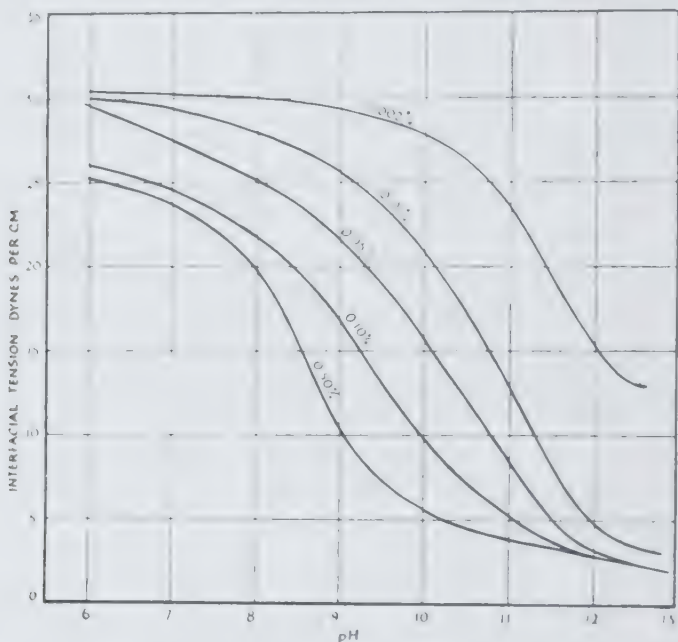


Fig. 43.—Effect of pH on interfacial tension of various concentrations of sodium oleate against xylene

of grease on the parts being cleaned. The maximum charge on the particles is found at a comparatively low concentration of alkali (approximately corresponding to N/1000 NaOH), so that increasing the concentration of the latter results in two opposing effects, viz. reduction of surface tension and simultaneous decrease in the charge of the emulsified globules. This may account for the good emulsifying properties of some of the milder alkalis and for their effectiveness at low concentrations. Excessive alkali concentrations and high pH may result in breakdown or instability of the emulsified grease, due to the reduction in the electro-static charge on the particles.

In order to promote the peptisation and emulsification of oils and greases, the cleaning solution should have a relatively low surface tension; unfortunately, however, solutions of the common alkalis have relatively high surface tensions (see Table XXVI).

TABLE XXVI
SURFACE TENSIONS OF SOME ALKALINE SOLUTIONS

Alkali (2 per cent solution)	Surface tension (20 C.) dynes per cm.
Water	72.8
Sodium hydroxide	77.0
Sodium carbonate	77.0
Trisodium phosphate	76.2
Sodium silicate	76.3
Sodium aluminate	75.6
Soap	28.0

It will be seen that soap solutions have a considerably lower surface tension than have solutions of alkalis; this is the case even when the soap is present in very small concentration. For this reason soap is a very useful constituent of an alkaline detergent, and even when it is not deliberately added a certain amount of soap gradually forms, due to the saponification of the oils and fats. In fact, this beneficial action of soaps has been recognised by electro-platers for a long time, and it used to be the practice to put a small amount of solution taken from an old bath into freshly made cleaners, as it was found that the new solutions would work better with such an addition.

Soap has the disadvantage of being precipitated by the calcium and magnesium salts present in hard water. This precipitation not only results in the removal of the soap from the solution, but also in the deposition of insoluble scums on the metal surface which are very difficult to remove.

Similar considerations apply to the possible presence of heavy metal compounds, which result in the precipitation of insoluble metallic soaps. The addition of materials, such as "Calgon" (sodium hexametaphosphate) is useful in this connection. "Calgon" prevents the precipitation of insoluble soaps even when present in quite small amount in hard water, so that soaps can be used successfully without danger of their being thrown out of solution. Soap suffers also from the limitation that at a pH of below 10.2 approximately it begins to decompose; this does not matter in the case of highly alkaline cleaning solutions, since the soap solutions are perfectly stable at pH values in excess of this figure, but when mild alkalis are being used with metals such as zinc or aluminium, for instance, this instability prevents their effective use.

It is likely that the presence of a soap or a wetting agent (see p. 154) not only assists in the wetting of the oil film directly, but also facilitates peptisation of the contaminant and the stabilisation of the resulting emulsion. It was found by Millard⁽⁹⁾ that the addition of alkalis to soap solutions decreases their surface tension when measured against benzene; the effect of caustic soda is the most pronounced, trisodium phosphate and sodium silicate having comparatively little influence (see Table XXVII).

TABLE XXVII
SURFACE TENSION OF ALKALIS IN SOAP SOLUTION AGAINST
BENZENE (40°C.)

Alkali	Percentage alkali on 0.03 per cent soap solution								
	0	0.006	0.012	0.024	0.03	0.048	0.06	0.09	0.096
NaOH . .	26.8	19.1	14.1	7.1	—	—	—	—	—
Na ₂ CO ₃ . .	26.8	23.4	20.0	18.8	—	14.6	—	—	7.9
Na ₃ PO ₄ . .	26.8	—	—	—	20.0	—	16.8	13.7	—
Sod. silicate* .	26.8	—	25.8	25.3	—	24.3	—	—	22.9
Sod. silicate† .	26.8	—	25.0	23.0	—	20.9	—	—	18.6

* Containing 10.5 per cent Na₂O and 26.70 per cent SiO₂.

† Containing 20 per cent Na₂O and 30 per cent SiO₂.

Cleaning Efficiency.—Fall⁽¹⁰⁾ reviewed the theory of the detergent action of soap solutions and also carried out investigations on the cleaning of artificial soils in the form of suspensions of finely divided manganese dioxide. This material was selected because, though free from grease or oil, it forms adherent smudgy deposits, which cannot be readily removed by the action of water alone. Suspensions of MnO₂ in water are stable, whilst the material can be washed away with the aid of soap or alkaline solutions. It is also insoluble in the detergent solutions and, moreover, the amount of the manganese salt present at any stage can readily be determined chemically.

The amount of manganese remaining unpeptised after a given cleaning cycle was determined by the following procedure: to 1 gm. of manganese dioxide in a 100-c.c. flask was added 50 c.c. of the detergent solution and the flask shaken mechanically for five minutes at 130 shakes per minute. It was then placed in a thermostat for four hours, the two temperatures selected for the investigation being

40° C. and 75° C. respectively. At the end of this time a 25-c.c. sample of the solution was withdrawn and the manganese dioxide present determined. This figure in gm. MnO_2 per litre was termed the "MnO₂ value" of the detergent, since it was assumed that the greater the peptising action of the detergent solution, the greater would be the amount of manganese dioxide suspended in the solution.

It was found that the relative detergent values of soaps differ with different types of soil due to the specific absorption characteristics of the solution. The relative detergent powers of a number of standard concentrations of different soaps at 40° C. and at 75° C. show that an optimum concentration for the maximum detergent action exists. This lies within the range 0.2 to 0.4 per cent and is independent of the type of soap used. The MnO_2 values for some alkalis are shown in Table XXVIII; low surface tension of the solution does not necessarily mean that it will have good detergent properties.

The excellent peptising properties of sodium silicate ($\text{Na}_2\text{O}_4\text{SiO}_2$) are worthy of note. It was found that silicates are similar to soap so far as the MnO_2 value is concerned, with an optimum concentration at 0.0125 to 0.05 per cent; at concentrations greater than 0.15 per cent, however, the high silica low alkali silicates are preferable. For purposes of comparison the MnO_2 values of some tallow soap solutions are shown in Table XXIX.

Effect of Temperature. Another interesting aspect is that at lower temperatures the detergent characteristics of the solutions are generally improved. This is apparently contradictory to the common

TABLE XXVIII
MnO₂ NUMBERS OF ALKALINE SOLUTIONS (FALL)

Alkali per cent	NaOH		Na ₂ CO ₃		Na ₃ PO ₄		Na ₂ O ₄ SiO ₂	
	40° C.	75° C.	40 C.	75 C.	40° C.	75 C.	40 C.	75° C.
0.5	0	0	0	0	0	40	292	240
0.3	0	0	0	0	0	140	382	261
0.15	17	52	0	12	70	274	396	287
0.05	232	231	30	99	350	290	434	346
0.025	347	269	110	196	365	291	445	351
0.0125	373	252	254	234	273	248	436	348
0.0062	333	140	203	140	125	113	427	216
0.0031	17	—	68	17	40	0	278	0
0.0015	—	—	0	0	0	0	36	0

TABLE XXIX
MnO₂ NUMBERS OF TALLOW SOAP SOLUTIONS

Soap concentration per cent	40° C.	75° C.
2.0	327	316
1.4	427	372
0.8	496	433
0.4	532	455
0.2	539	460
0.1	328	322
0.05	334	123

practice of using such solutions at high temperatures; in fact, many manufacturers of cleaning compositions recommend that the solutions be used at temperatures as near as possible to the boiling-point. The reason for this apparent discrepancy is perhaps to be found in part in the fact that in the case of cleaning in still tanks the use of a hot solution results in the formation of convection currents, and these are undoubtedly of considerable importance in the cleaning action of the detergent. In actual practice, therefore, the mechanical value of these convection effects will undoubtedly outweigh any advantages a solution of lower temperature might have. In the experiments quoted the rapid shaking provided the mechanical action promoting removal of the contaminant. Fall's work suggests, however, that in some instances where a substantial proportion of solid matter is present, the use of a lower temperature might be worth experimenting with where good movement between the parts to be cleaned and the solution can be brought about. These conditions prevail in pressure spray-washing machines, for example.

WETTING AGENTS

Wetting agents are nowadays being increasingly used in alkaline detergents, on account of their valuable properties in promoting emulsification and in reducing the surface tension of solutions of alkalis, which, as we have seen, are not appreciably lower and are sometimes higher, than that of water.

Synthetic wetting agents are not, in general, seriously affected by the presence of heavy metal or alkaline earth compounds, and are stable even in acid solution. A very large number of wetting agents are now available under different commercial names, but it is to be

borne in mind that not all are suitable for use in alkaline detergents. Some tend to be unstable and are precipitated out, whilst others may undergo decomposition under the pH conditions prevailing in the detergent solution. Careful selection of wetting agents is therefore essential.

The materials employed generally consist of a long hydrocarbon chain molecule, to which is attached a water-attracting group, of which the most important are the $-\text{OSO}_2\text{ONa}$, $-\text{COONa}$, and SO_3Na groups. A proper balance in the molecule must exist between the water-attracting or polar group and the hydrocarbon group, as, if the former predominates excessively, the material will lack surface-active properties, and, if the latter, the compound will not be sufficiently water-soluble to be of value. Generally these materials have a molecular weight of the order of 300-350, and contain a hydrocarbon chain of at least eight carbon atoms. For good detergent properties a fairly long chain containing at least twelve carbon atoms is necessary, although good wetting properties are obtainable with considerably shorter chains.

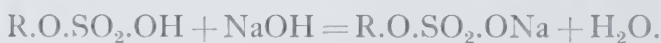
When a surface-active agent of this description exercises its function in promoting the wetting of oil, the molecules of the wetting agent orientate themselves in such a way that the polar groups are in the aqueous portion of the mixture and the hydrocarbon chain is in the non-aqueous liquid. In the case of solid particles, the hydrocarbon group is adsorbed at the surface of the solid in a similar manner. This phenomenon finds larger scale practical application in the flotation processes for the concentration of mineral ores.

The sodium and potassium salts of the long-chain fatty acids having eight or more carbon atoms all have surface-active properties and constitute the soaps whose detergent properties have been known from very early times. The solubility in cold water decreases, as the length of the hydrocarbon chain increases. Thus, sodium stearate, having a C_{18} carbon chain, is practically insoluble in cold water. The introduction of a double bond into the molecule increases the solubility, however, as is the case with sodium oleate, for example. The solubility increases rapidly as the temperature is raised, however, so that when these soaps are used in warm or hot water, as is the common practice, the solubility is adequate for them to exhibit excellent detergent qualities. On the other hand, even the soaps of acids within the C_{12} to C_{18} range may have poor detergent properties if the molecule is not suitably balanced; thus, the soaps of linoleic acid and ricinoleic acid (both C_{18} unsaturated fatty acids) are good wetting agents, but are poor detergents.

Materials Used. Perhaps the earliest and best known of the wetting agents is Turkey Red Oil, which is sulphonated castor oil. This product has its limitations, as it is difficult to manufacture a uniform product, whilst the material is inferior to soap both as regards wetting and detergent properties. The next group to be used was the sulphated fatty alcohols, such as lauryl and cetyl alcohols. The alcohols themselves are produced by the catalytic reduction of the corresponding fatty acid, after which sulphation is carried out. The reactions concerned may be represented as follows:



On treatment with caustic soda the sodium salt is formed:



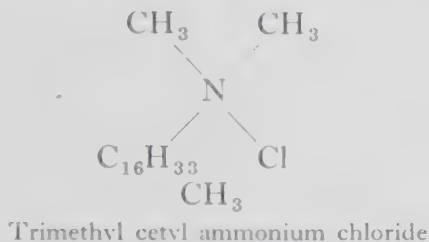
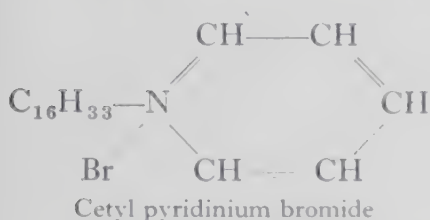
R may be any type of fatty alcohol radical such as lauryl, myristyl, etc.

These alkyl sulphates are stable in neutral or even in acid solution and are essentially similar to soap in chemical structure, apart from the fact that the $—COONa$ group of the soap is replaced by the $—O.SO_3Na$ group. It is thus seen that these materials are produced from natural oils and fats by a fairly lengthy process, which makes them relatively costly. It is therefore of interest to note that it has recently been found possible to use ethylenic hydrocarbons resulting as by-products in petroleum refining as the starting-point in the manufacture of detergent products of similar composition. Excellent materials are now commercially available. Other classes of compounds have been developed in recent years, and the principle involved in the action of these is similar to that which has already been described.

The sulphonated alkyl-aryl compounds are worthy of mention. These have a sodium sulphonate group attached to an alkyl substituted aryl group (e.g. the Perminals). This group of compounds is characterised by its high surface tension depressing properties; their detergent value is, however, poor, and they do not foam readily. Sulphonated amides, of the general structure $R.CO.NH.C_2H_4.SO_3Na$ (where R is an alkyl group) are also good wetting agents, but are not very stable to strong alkalis. Amongst the most effective of the surface tension depressants are the esters of the sulphonated dibasic acids, such as succinic acid. They do not give stable foams, and their detergent properties are not high.

Cation-active Compounds.—One group of substances which differs inherently from the alkyl sulphonate type is the group of

cation-active compounds. Here the molecule ionises in such a way that the greater part of it carries a positive charge, the negative ion, which may be a halide, for example, being relatively small. Practically all surface-active compounds ionise slightly in solution, and those that have been considered so far are anion-active, i.e. the organic portion of the molecule is discharged at the anode when the solution is subjected to electrolysis. The cation-active substances are not so commonly employed; typical of materials in this group are the quaternary ammonium compounds and the primary and secondary amine acid salts. These cation-active materials are especially useful in neutral or in acid solutions where they possess excellent detergent, peptising, and emulsifying properties. One advantage of the cation-active materials is the fact that they will not react with compounds of the heavy metals. Typical chemicals of this group are:



It is important to note that anion-active and cation-active materials should not be mixed, as they may mutually interact with the precipitation of an insoluble compound. Furthermore, in the case of electrolytic cleaning (see p. 161), an anionic compound would prove more effective when anodic cleaning is used than would a cation-active material, and vice versa. Another factor that has to be considered is whether a cation-active material, for example, might be precipitated at the cathode due to the neutralisation of the charge on the non-polar ion, especially if the acid is insoluble (only the sodium salt actually used being soluble), as is not infrequently the case.

Wetting agents, unless they are liquids, can be conveniently included in appropriate proportion in compounded cleaners supplied in powder form. The correct amount can then be added by the manufacturers. Alternatively, when cleaners are being made up by the user the wetting agent can be added to the solution before use, and in such cases liquid materials can be conveniently employed. It is found in practice that there is an optimum concentration of surface-active agents beyond which further addition has no appreciable effect in bringing about greater reduction in surface tension. For most

materials 0.1 to 0.3 per cent of wetting agent is the maximum that need be added. Fig. 44 shows the relation between surface tension and wetting agent concentration in 4 per cent caustic soda solution at 20° C. for five typical wetting agents. Tergitol 7 is an alkyl compound in which the active $-\text{SO}_3\text{Na}$ group is attached to the middle of the molecule; it is represented by the formula:

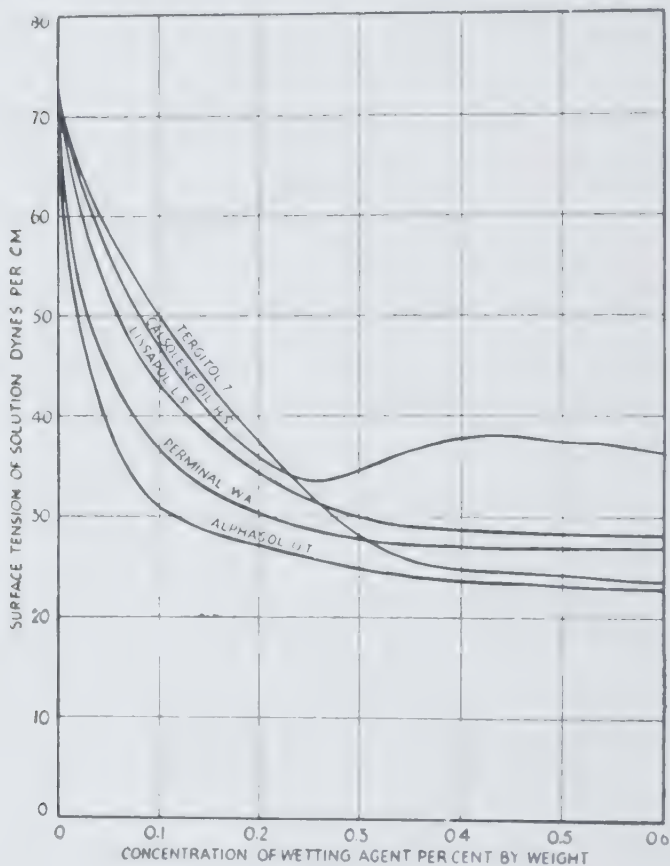


Fig. 44.—Effect of wetting agents on surface tension of 4 per cent sodium hydroxide solution

Calsolene oil HS and Lissapol LS are of the sulphated fatty alcohol type; Perminal WA is a sodium naphthalene sulphonate, whilst Alphasol OT is the dioctyl ester of sodium sulphosuccinic acid.

The concentration of wetting agent should be kept as low as possible, consistent with good wetting properties; it is often found that increasing the concentration results in the formation of residual films on the metal surface which may interfere with subsequent

processes. These films are especially liable to form if wetting agents which are not sufficiently stable to the alkali are used; in such cases decomposition products are formed which may adhere to the metal surface very tenaciously. The rinsability of a wetting agent depends both on its solubility and its molecular structure. Clearly, the more strongly surface-active the compound is, the more difficult will it be to rinse off.

The use of wetting agents in cleaners has been discussed by the author.⁽¹¹⁾

Testing of Cleaners. The evaluation and testing of cleaning solutions and compositions are not easily carried out. Perhaps the simplest method consists in suspending a plate as uniformly coated as possible with the oil or contaminant which it is desired to remove in the detergent solution. The time which elapses before it can be lifted out without evidence of a "water-break" on the surface is a measure of the effectiveness of the cleaner. When cleaning is complete, the solution will run uniformly from the metal surface without the formation of globules or rivulets. With a little practice, reasonably accurate comparisons of cleaning times can be made.

The "water-break" method has, however, been criticised on the ground that not only is the break dependent on the thickness of the water film, but also false water-breakless surfaces can be obtained as a result of preferential adsorption of hydrophilic material.⁽¹²⁾ The adsorbed material can be removed by a dip in a 5 per cent solution of sulphuric acid; alternatively an acidified copper sulphate solution can be used for dipping the test piece into after cleaning as copper will then be deposited only on the chemically clean areas. The latter technique enables a quantitative estimate of cleaning properties to be made by measuring the areas covered by the immersion deposit of copper. By determining the time required for cleaning with different solutions the relative merits of detergents can be evaluated.

More recently the use of oil carrying a fluorescent dyestuff to indicate when cleaning is complete has been described. After immersion in the cleaner for a given time the plates are examined or photographed under ultra-violet light, and since the amount of fluorescence is proportional to the quantity of oil adhering to the metal surface a rapid and convenient method of judging the efficiency of a metal-cleaning compound is provided.

As a result of tests carried out using the fluorescent method of evaluating cleaners, it was found by Morgan and Lankler⁽¹³⁾ that Nacconol NR (a proprietary wetting agent of the long chain alkyl-aryl sulphonate type) reduced the time required by various alkaline

cleaners to remove oily contamination from metal surfaces. Thus it was found that using a 10 per cent solution of a cleaner consisting of:

Caustic soda	.	.	.	.	10 per cent
Trisodium phosphate	.	.	.	.	55 "
Soda ash	.	.	.	.	35 "

at a temperature of 140 F. fluorescence was still evident after ten minutes, showing incomplete removal of the oil. In the presence of 5 per cent of the wetting agent, however, a 2 per cent concentration of this cleaner effectively removed the oil in ten minutes. Sodium metasilicate solution under similar conditions effects almost complete removal of the oil when it is used alone; the addition of a 5 per cent solution of the wetting agent resulted in complete removal in two to four minutes. A 1 per cent solution of the mixture completely removed the mineral oil in eight minutes, although a 4 per cent solution of metasilicate alone did not bring this about in ten minutes. Experiments carried out on metals other than steel showed similar results; the cleaning of aluminium and galvanised iron was especially favoured by the presence of the wetting agent, but with brass and tinplate, cleaning took place rather more slowly than with steel, although the presence of the Nacconol NR exercised a favourable influence.

A useful method of testing has been termed the "residual soil" method which can be applied both for the evaluation and routine testing of cleaners. The test pieces are first subjected to the cleaning solution, carefully rinsed and dried and then weighed. The residual contaminants are then washed off by treatment with petroleum ether, after which the specimen is rinsed with alcohol, dried and reweighed. The amount of contaminant found in this way is a direct measure of the cleaning efficiency of the detergent solution. It is claimed that this method will indicate residual contamination of the order of 0.1 to 0.2 mgm. for a test panel of 13 sq. in. total area and will give no change in weight for such a test panel if it has been chemically cleaned.⁽¹⁴⁾

In another method⁽¹⁵⁾ steel test panels which have been subjected to a standard contaminating and cleaning cycle are rinsed in running water at 50° C. for five minutes to eliminate false water-breaks and then sprayed with clean water by a fine atomiser. Any residual oily areas are shown up as a spray pattern by this method, and the area of this pattern can be estimated. Again, this gives a quantitative measure of the efficiency of the cleaner which has been termed the "cleaning index".

The control of alkaline cleaners in actual use is most difficult, if

not impossible, to carry out. pH and active Na_2O determinations are of some value, but solutions must be discarded when they begin to contain any substantial amount of emulsified oil and dirt. There is no ready means of determining this, apart from the actual performance of the cleaner, and a fresh solution must be made up when its effectiveness appears to be reduced.

Detergent Properties. The most highly surface-active compounds are not necessarily the most effective detergents; a good detergent must not only be capable of lowering the surface tension, but must also have good deflocculating and emulsifying properties. According to Hartshorn,⁽¹⁶⁾ good detergent surface-active materials are characterised by relatively simple, long chain, non-polar groups with powerful polar groups, such as the carboxyl group (sodium salt). This accounts for the excellent detergent qualities of soap, which is one of the best detergents available, and the application of which is only limited by the factors already mentioned (e.g. precipitation by calcium, pH limitations, foaming qualities, etc.).

ELECTRO-CLEANING

The use of electrolytic alkaline cleaners is now very common practice in connection with electro-plating processes. Fundamentally, electrolytic cleaning consists in suspending the articles to be cleaned in an alkaline solution and making them one electrode in a direct current circuit. An applied potential of 6 to 12 volts may be used, and the articles are generally made the cathode; the cathodic current densities employed range from 30 to 100 amps. per sq. ft. A considerable volume of hydrogen is liberated by the current at the surface of the work being cleaned, and this gas formation effectively cleans the metal surface by its mechanical scouring action, which expedites the work of the alkaline solution.

Free alkali is formed at the cathode during electrolysis, and it has been suggested that this plays a part in promoting saponification of grease. This, however, is probably unlikely in view of the fact that saponification is a relatively slow process, whilst electrolytic cleaning takes place quickly and is about as effective with non-saponifying oils as it is with saponifiable greases.

The tank may be made the anode, but it is preferable to use separate anodes, in order that the current densities should be more readily controllable. Nickel forms an ideal metal for anodes, as it is neither filmed nor attacked by the solutions used.

Cathodic cleaning is preferred because twice as much gas is liberated at the cathode as at the anode (where oxygen is evolved),

so that a more rapid cleaning action might be expected. In actual practice, however, this difference in the effectiveness of cathodic as opposed to anodic alkaline cleaning is by no means as marked as might at first sight appear. On the other hand, cathodic cleaning has the disadvantage that should any traces of soft metals become dissolved in the solution these will be deposited on to the work (forming the cathodes) by the current; there is also the possibility that hydrogen absorption may take place in some circumstances⁽¹⁷⁾ with the possible consequent hydrogen embrittlement of steel parts. (See p. 53.)

If anodic cleaning is to be used, however, even for a very short time, great care must be taken to ensure that attack of the metal by the alkali does not take place. Some metals are very readily dissolved under anodic conditions; this applies particularly to zinc and aluminium.

The plating out of dissolved metallic impurities on the cathodes is overcome in some plants by the use of a reversing switch, which enables the current to be reversed momentarily just before the cleaned articles are to be removed from the tank. Thus, any metallic films which may have been deposited are re-dissolved. This procedure is not essential, however, and a great deal of large-scale cleaning on sensitive metals, such as zinc alloys, is carried out without the use of a reversing current. The films which may be deposited are very thin and can be removed by subsequent operations after cleaning, such as a quick immersion in cyanide solution, or in a weak hydrochloric acid or sulphuric acid dip.

Where sensitive metals are to be cleaned prior to plating in organic types of bright nickel solutions electrolytic alkali cleaning should always be anodic. Zinc-base alloys and brass must not be subjected to a final cathodic alkali treatment if good nickel deposits are to be obtained.

Operating Conditions.—Electrolytic cleaners are commonly used hot, and the tanks can be arranged with a suitable overflow to enable surface grease accumulations to be readily skimmed off. In composition, the solutions do not differ substantially from those employed in non-electrolytic cleaning processes. The desirability of a high electrolytic conductivity must, however, be borne in mind in formulating them. For this reason soaps are not favoured as ingredients owing to their poor conductivity, while the use of elevated temperatures, relatively high concentrations and solutions of high pH value all favour increased electrical conductivity. Thus, between 20°C. and 100°C. the conductivities of 3 per cent solutions

of most of the common alkalis increase between two and a half and four times. Cleveland⁽¹⁸⁾ has determined the electrical conductivity of some alkaline solutions over a range of temperatures; the results are calculated on a relative scale as the conductivities of the solutions in amps. per sq. ft. of electrode area per linear ft. of distance between the electrodes. The potential used was 6 volts,

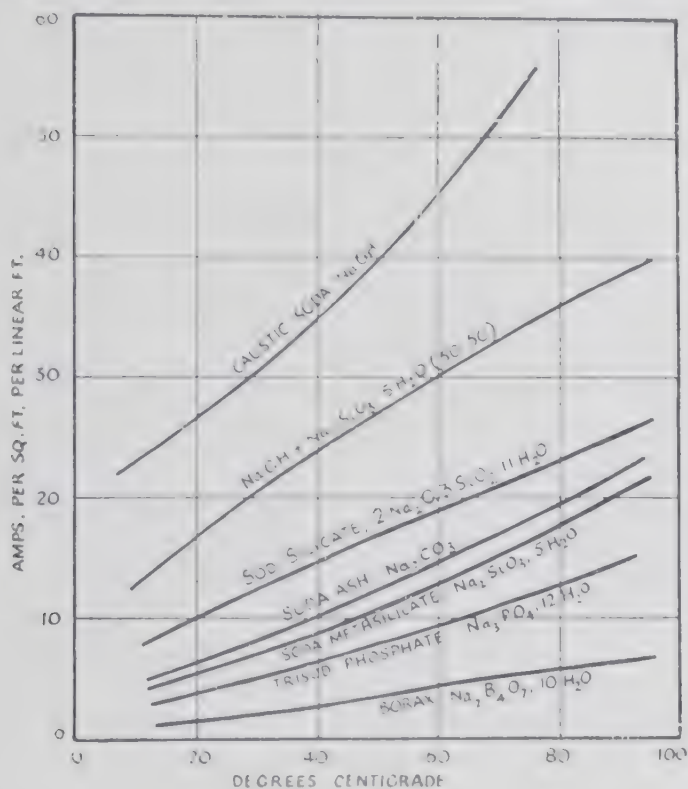


Fig. 45.—Comparative conductivities of 3 per cent solutions of commercial alkalis

and the electrodes were iron, 3 in. by 3.5 in., each cleaned by sand-blasting and placed 3.5 in. apart. Fig. 45 is based on some of the results obtained.

Caustic potash is sometimes favoured in electro-cleaners in preference to caustic soda on account of the higher conductivity of its solutions at all concentrations. The maximum conductivity of a solution of caustic potash occurs at a concentration of approximately 6 gm. equivalents per litre, whilst with caustic soda the maximum is at about 4 gm. equivalents.

Combined coppering and cleaning solutions are still in use, although they are not looked upon so favourably now as they were

at one time.⁽¹⁹⁾ These alkaline solutions contain a small concentration (about 1 oz. per gallon or less) of copper cyanide, together with some sodium cyanide. The theory of their action is that copper will deposit as a very thin film on those areas which have been cleaned by the alkali and the mechanical action of the hydrogen evolved; when the metal is entirely covered with copper it can then be assumed that cleaning is complete. The copper deposit acts as a basis for subsequent electro-deposited coatings. In practice, it is found, however, that the copper deposit can form on surfaces which are far from perfectly cleaned; such deposits will look satisfactory to the eye, but their adhesion may be very poor, so that plating will readily peel off. The method is sometimes used for coppering in the production of an "oxidised" finish.

Wetting agents are not commonly employed in electrolytic cleaners; some of the difficulties that may arise with them under the influence of electrolysis have already been discussed. If it is intended to include them they must be carefully selected and used with discretion on account of their foaming propensities. This foaming can become quite troublesome even with ordinary cleaner formulations on account of the high rate of gas evolution at the cathode. The hydrogen may also accumulate in the foam, with the result that a minor explosion can take place when the gas is ignited by the spark which occurs when the work is removed from the cathode bars. Addition of insoluble polar materials in emulsion form (e.g. hexyl or octyl alcohol) has been recommended for inclusion in the solutions to reduce foaming, but their use presents disadvantages, as they are relatively volatile and, therefore, vaporise off when used in hot solutions.

Cold-rolled Steel.—The increasing use of cold-rolled steel presents a formidable problem in metal cleaning on account of the tenacious nature of the films which may form on the metal surface under some conditions of rolling. Palm oil is perhaps the most commonly used lubricant in rolling-mill practice, and under the influence of heat and pressure, decomposition of the oil takes place with the liberation of free fatty acids which attack the surface. Palmitic acid can form gummy insoluble deposits of iron palmitate under such conditions. When soluble oils are employed as coolants they become overheated and will tend to char and oxidise; being in an emulsified form, oxidation is especially prone to take place with such oils owing to the large surface area of the minute globules which are exposed to the air. The oils and emulsifiers present form decomposition products, which are very strongly adsorbed at the metal

surface. The steel surface can act as a catalyst in such oxidation processes.

Similar contaminations can occur with the lubricants used in deep drawing and pressing operations and such deposits are equally difficult to remove. The trouble is enhanced if the metal is bright annealed in oxygen-free atmospheres.

Automatic Strip Cleaning.—Lyons⁽²⁰⁾ maintains that the removal of the coolant used in the rolling of steel strip is very difficult if carried out after annealing; steel strip should, therefore, be cleaned

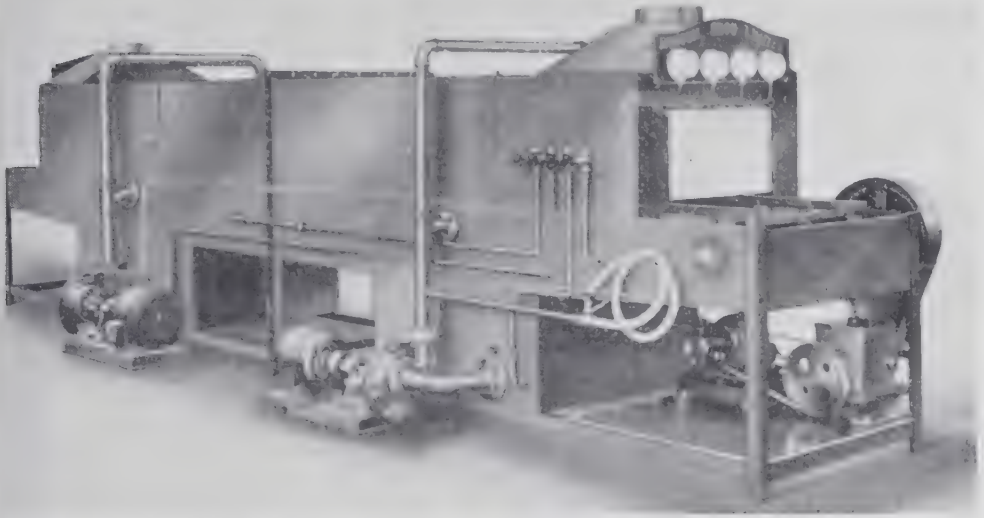


Fig. 46. Two-stage pressure washing machine for washing and rinsing aircraft cylinder blocks

[Courtesy of Dawson Bros. Ltd.]

for hot tinning before this latter operation. Unless the metal surface is scrupulously clean, pin-holes and discontinuities are liable to be present in the tin coating. The standard of cleaning required for hot tinning is, however, not so high as that necessary for electro-tinning, particularly where acid plating solutions are employed.

The method described for the cleaning of the strip consists first in subjecting it to heavy jets of warm alkaline solution to remove the main part of the oil present. The oil which is removed is skimmed from the surface of the spray tank from time to time. Next, the strip passes to the electro-cleaner, and then through water sprays and revolving brushes to remove alkali and smut. It is finally dipped in hot water to dry it, although for very high speeds, a hot air-blast drier, delivering air at 120°C. to 172°C., is found necessary. The clean dry steel is then ready for bright annealing, after which it is

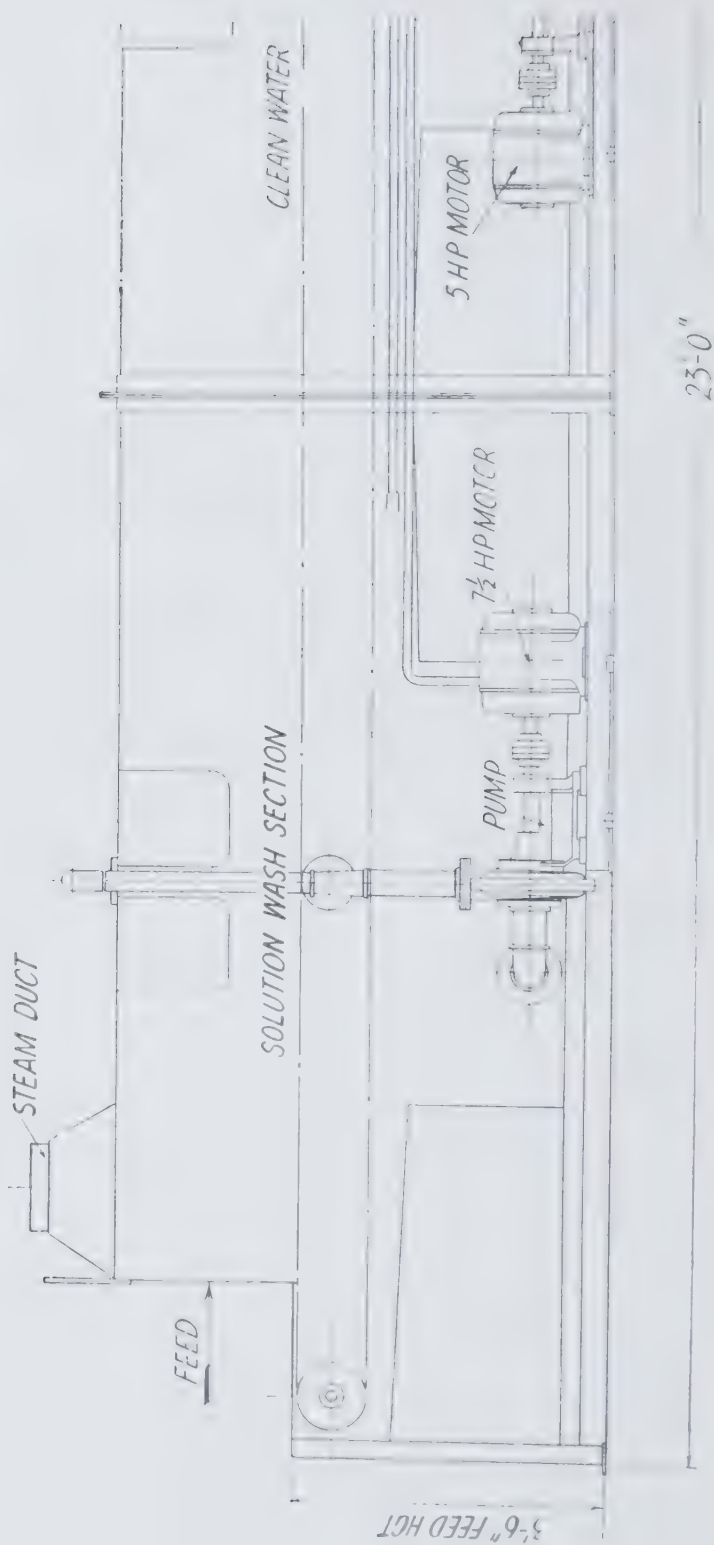


Fig. 47.—Conveyerised pressure spray washing machine

[Courtesy of Darson Bros. Ltd.]

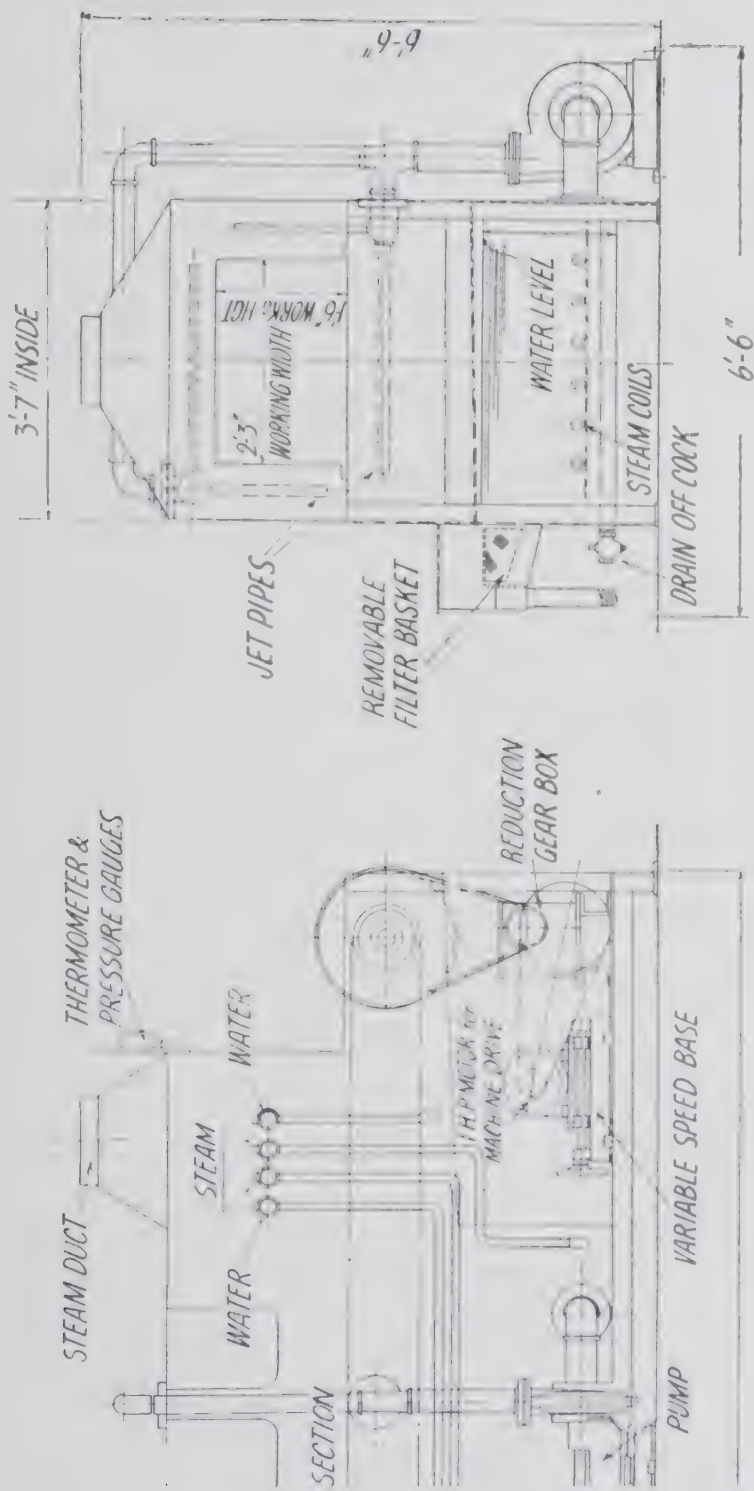


Fig. 47.—continued

put through a "skin-pass" under light pressure rollers. This operation requires no coolant so that no contamination occurs and the metal is ready for hot tinning.

The strip passes through the electro-cleaner at speeds of more than 1,500 ft. per minute, the treatment time being less than three seconds; it is connected to the current supply by means of contact plates, and is made the cathode, the current densities used being of the order of 50 to 100 amps. per sq. ft. The anodes are steel grids. The drag-out of solution from the cleaning tanks is very high under such conditions and rollers and air jets are employed to keep the losses small. The solution used in the electrolytic tank consists of either sodium metasilicate or phosphate in concentrations of 2 to 5 oz. gallon, although proprietary cleaners are also used. Silicates are considered especially suitable for work of this kind, with or without fortification by the addition of caustic soda. Palm oil is a saponifiable oil so that considerable quantities of soap accumulate in the solution with the formation of a good deal of foam. Successful methods of controlling this foam have not yet been worked out. In the spray tank foam is even more objectionable, as it deadens the action of the jets and interferes with cleaning. For this reason the alkali in the latter tank is kept relatively weak, a typical solution being one containing about 2 oz. per gallon of sodium carbonate; part of the carbonate may be replaced by trisodium phosphate.

Both the spray washer and the electrolytic cleaning solutions are maintained at a temperature of about 85°C.

ALKALI CLEANING PLANT

The plant used for the simplest types of alkali cleaning consists of tanks heated by steam, gas, or electricity, in which the parts to be cleaned are immersed in the solution either individually or packed in suitable baskets or in crates. These can be lowered by hand, using pulleys or by electrically operated gear. Electrolytic cleaning tanks are fitted with cathode bars, from which the work can be suspended. Arrangements may be made for circulating the solution, and an overflow at one end will help to remove surface grease accumulations. Where high temperature solutions are employed, exhaust ducting running along one or both sides of the tank (depending on its width) is very desirable to remove steam and maintain good working conditions.

Normally, alkaline cleaning solutions do not evolve noxious fumes, but where caustic soda is used in any proportion as a constituent of an electro-cleaner, the gas liberated at the electrodes results in some

caustic-carrying spray being carried into the atmosphere. This can be unpleasant and causes irritation to the mucous membranes of the nose unless a good exhaust is provided. In manually operated plants, splashes of the caustic solution can set up skin troubles, and in such cases it is preferable, if possible, to work with mixtures of alkalis free from caustic soda.

Alkaline cleaners (both of the electrolytic and immersion types) are nowadays commonly built in as units of automatic plating plants.

When steam coils are used for heating it is advisable to have them arranged vertically against one wall of the tank. The convection currents result in good circulation of the cleaning liquor, which,

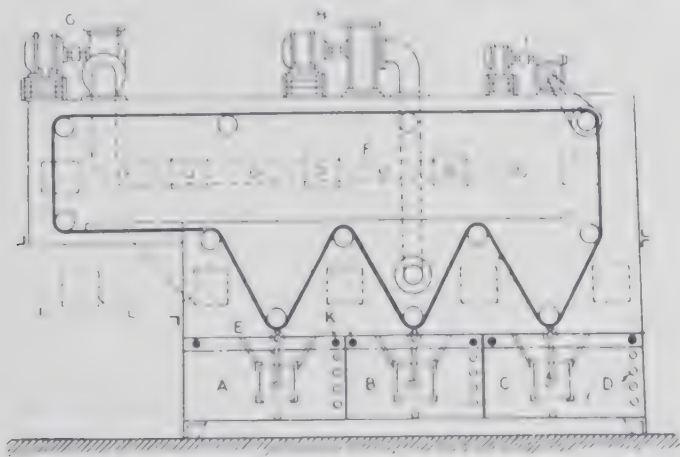


Fig. 48. Vertical conveyor plant for washing and drying delicate parts in baskets

- | | | |
|--------------------------|--------------------------|----------------------------|
| A—Washing section. | B—First rinsing section. | C—Second rinsing section. |
| D—Heating coils. | E—Conveyor. | F—Drying, cooling section. |
| G—Cooling device. | H—Vapour exhauster. | I—Conveyor device. |
| J—Loading-unloading end. | K—Sprayers. | L—Baskets. |

as has been seen, greatly facilitates the cleaning efficiency of the solution.

Conveyorised pressure spray washing machines are available, which have arrangements for projecting the hot alkali solution from a series of jets on to the parts to be cleaned. The usual types of alkaline solutions are employed with pressures of up to 40 lb. per sq. in. at the jets. The temperatures used are about 180° F, and the parts to be cleaned travel through the plant on a conveyor. The two-compartment types of unit are the most satisfactory, the second chamber using clean hot water only to rinse away alkali. Careful design and location of the jets are necessary to ensure that every part of the article being washed is reached by the solution. Fig. 46

shows a machine of this type for washing and rinsing aircraft cylinder blocks, the general mechanical arrangement being similar to that illustrated in Fig. 47.

Zinity⁽²¹⁾ describes some conveyerised plants used in the cleaning of metal parts.

In Fig. 48 is shown a plant for the washing of fuse and detonator parts and bullet jackets. The parts are very fragile and easily liable to damage, while the detonator parts are small and must not be mixed. The components travel in baskets, suspended from a conveyor which immerses them automatically and continuously in the different washing and rinsing solutions. The return travel of the baskets is accomplished in the upper part of the machine in a drying and cooling-off section. The baskets are normally of a standard size of 9 in. by 9 in. by 20 in., although this can be varied if required, and each contains a different type of part. Some baskets are specially designed with shelves and compartments to carry delicate threaded parts.

Plants have also been produced for the cleaning and pickling of components in the same unit. The highly corrosive nature of the conditions demands the most careful attention in the design of this type of plant.

A wide range of mechanised cleaning plants of all kinds is now in regular use in industry, and provided steps are taken to ensure that they are kept in good working order and that suitable alkaline solutions are employed for the work in hand, excellent results are obtained.

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METAL COLOURING:
DECORATIVE AND LIGHT-DUTY FINISHES

The colouring of metals by treatment in various solutions has been practised for centuries; in modern usage such colouring processes are applied largely for decorative purposes where it is desired to improve the appearance of a metal or to simulate a more costly metal, as in the bronzing of steel, for example.

Applications.—While metals may be coloured by the application of paints or lacquers the term “metal colouring” is usually applied to those processes in which the metal surface is itself treated, so that it develops a colour differing from that which it originally had. Such a conversion may only occur to a very small depth so that interference films are formed on the metal surface either by a chemical or an electro-chemical process. Interference films are very thin (250 to 550 Å.), and, although without colour themselves at this stage, they result in a coloured appearance of the metal surface, due to the mutual extinction of certain wave-lengths of light which are out of phase when reflection takes place from the metal and from the film surfaces. As the thickness of the film increases, the colours change from yellow to red, blue, and bluish green, after which the colour of the film itself becomes evident. If the film is non-uniform in thickness an iridescent or mottled coating will be formed.

General Methods. The finishes to be described are produced generally by one or other of the following means:

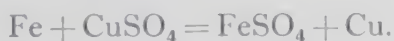
- (a) Treatment by immersion in or by rubbing or spraying with a chemical solution which converts the metal surface into one of its coloured salts (e.g. oxide, sulphide, etc.).
- (b) Heating in air or in a gaseous atmosphere to form a coloured oxide film of suitable structure and appearance.
- (c) Immersion in a solution of the salt of a metal higher in the electro-chemical series than that being treated, whereby a chemical exchange reaction occurs with the deposition of a film of the second metal on the first. Such a film may be metallic in appearance or not, depending on the form in which the latter metal is deposited.

- (d) Conversion of the metal surface to one of its compounds by electrolysis; an example of this is the anodic oxidation of aluminium, whereby the metal surface is converted to a tenacious film of aluminium oxide.

The appearance of finishes so obtained is greatly dependent on the initial surface of the metal being treated. The films are usually exceedingly thin (as has been pointed out), so that they accurately reproduce the surface condition of the underlying metal. Thus, entirely different effects result from the same colouring treatment, depending on whether the metal has been pre-treated by acid-dipping, shot-blasting, scratch-brushing, etc. The coloured film may be altered by rubbing with wet pumice or by polishing to "relieve" the high lights of the article.

Combined electro-plating and colouring processes are often employed. This is especially the case with steel objects, which are commonly electro-plated with copper from a cyanide solution, the latter metal then being coloured. Copper is chosen because it is easily treated to give a variety of pleasing colours, as will be described later.

The processes of deposition of metals on to other metals by immersion are typified by the copper coating produced on steel when the latter is immersed in a solution of copper sulphate. A simple chemical exchange takes place:



Such deposits are relatively thin and have poor adherence.

In other cases, as when zinc is immersed in nickel sulphate solution, the nickel is precipitated in a finely divided form so that a black finish results instead of a bright nickel deposit. This fact is made use of in the application of black finishes to zinc.

As a general rule, the coatings to be described in this section have relatively low durability and are unsuitable for exposure to severe atmospheric conditions for any length of time. They are therefore commonly lacquered with a nitro-cellulose or other transparent lacquer to improve their weathering qualities. Alternatively, they may be oiled or waxed if they are of a porous type or impregnated with a variety of different substances to obtain a satisfactory finish.

In some instances, colouring plays an important part in the finish, as in gun blackening. Here it is essential to darken the steel to avoid reflection of light which would render the weapon unduly conspicuous.

As colouring processes often add little to the corrosion-resistance of the metal to which they are applied, they are most useful on parts

which are to be employed under indoor conditions, or, as in the case of rifles, on parts which are kept oiled and frequently cleaned.

Some colour finishes (for example, the oxide coatings on steel applied either by heat or by one or other of the chemical treatments to be described) are very useful on account of the hard surface which they give. These finishes are not easily scratched or damaged, despite the fact that they do not withstand weathering or corrosive conditions well. Thus they are useful on parts and fittings for indoor service which are subject to much handling, such as small tools. In this respect they are superior to organic finishes and to phosphate coatings.

Finishes of this group can be applied by chemical immersion treatments, using a great variety of solutions. The published formulae of solutions employed run literally into thousands. Some of these give good finishes, but many also give indifferent results, since they were probably designed for a specialised application under conditions which may not be universally reproducible. Other solutions are either too critical in their working conditions or they demand a particular grade of metal or surface finish for satisfactory results to be obtained. It is not proposed here to add to the multitude of formulae, so that only details of the well-established methods will be given. Some of the more complex formulae which have been published from time to time appear to have been developed empirically, since it is evident that not all of the ingredients perform a useful function in the solution.

Immersion Deposits of Nickel.—Nickel can be deposited on steel by simple immersion in a weak solution of nickel sulphate or nickel ammonium sulphate for 5 to 10 minutes. The solution contains 1 to 2 oz. per gallon of nickel sulphate and often a little boric acid to maintain the pH at around 3 to 4. The solution is used at a temperature of 160 F. to 180 F. The deposit obtained is very thin, and somewhat variable. The process is chiefly used on very cheap articles as a finish or as a pre-treatment before vitreous enamelling. For the latter purpose a nickel thickness of only 0.000002 in. to 0.000005 in. is required for maximum adhesion. After treatment the metal is rinsed in a dilute carbonate or cyanide solution to prevent rusting prior to enamelling.

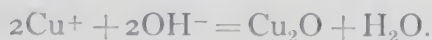
Somewhat heavier immersion deposits have been obtained⁽¹⁾ by immersion in a solution of:

Nickel chloride	.	.	.	600 g. l.
Boric acid	.	.	.	30 g. l.

The pH is 3.5 to 4.5 and the temperature used is about 160°F. The work is preferably agitated. Cleaning is carried out by scouring or cathodic alkaline treatment. Acid pickling is not too satisfactory unless followed by scouring and alkaline treatment as it seems to set up large anodic areas leading to uneven sporadic nickel coatings. Deposits up to 0.0003 in. in thickness can be obtained in this way. The deposits are of low protective value in themselves, but are suitable as a basis for subsequent organic coatings, enamelling, etc.

“Electro-colour” Process.—Of recent years a new method of applying coloured coatings has been developed, and consists of an electro-deposition process whereby thin films of metallic oxides are deposited, which exhibit different colorations according to the conditions of deposition. Films of this type can be obtained by depositing copper from a copper lactate solution. Some very attractive finishes can be obtained in this way, but, again, their durability is low and they must be lacquered if useful service is to be obtained.

Stareck⁽²⁾ describes the “Electro-colour” process in which an organic copper solution is employed. Plating is carried out in the normal manner, using a voltage of about 0.5 volt and a cathode current density of $\frac{1}{2}$ to 3 amps. sq. ft. The deposit consists of copper oxide, Cu_2O , produced by reduction at the cathode:



The colours result from interference tints in the thin oxide film and the colour obtained depends on the current density, composition, and temperature of the solution, and especially on the duration of plating. As the film thickens, its colour changes through the spectral range after which the cycle starts again. As many as fifteen cycles can be gone through; with each succeeding cycle the colours become less brilliant, although the film is thicker and hence more durable.

The solution is claimed to have a remarkable throwing power, and the cathode efficiency is said to be 100 per cent.

While the colours are very attractive and remarkably uniform, it is, however, rather difficult to maintain a standard colour from the bath, and this militates against the use of the method for mass production. It is best suited to individual specialised articles where an attractive finish is required.

TREATMENT OF STEEL AND IRON

Temper Colours.—The most important of the coloured finishes applied to ferrous metals are the blackening processes. For many

applications a dark finish on steel is required for decorative purposes, while for military equipment a durable black finish is essential to avoid light reflection from the metal surface.

When ferrous metals are heated in air a range of colours is produced, varying from yellow through orange to dark blue, depending on the temperature and the duration of heating. These colorations are due to the formation of oxide films on the metal surface and the colour is a result of interference tints which are developed within the thin oxide layer. The higher the temperature of treatment, the thicker is the oxide layer; the thicker coatings are more durable than the thinner ones. Thus, if steel be kept at the same elevated temperature for a period, the colour produced on the surface will change progressively as the film thickens. Table XXX shows the approximate nature of the colours formed on carbon steel when it is heated up gradually in air. These "temper colours," as they are called, are normally formed on metals in the tempering process, but in order to produce thicker or more uniform oxide coatings, steel parts are often dipped in oil prior to heating. Tallow or linseed oil are commonly employed in gun-browning, the grease being applied as a thin film to the parts, after which they are heated for about

TABLE XXX
"TEMPER COLOURS" PRODUCED ON STEEL BY HEATING
TO VARIOUS TEMPERATURES

Temp. °C.	Temper colour
220 . . .	Pale straw
230 . . .	Straw
240 . . .	Dark yellow
250 . . .	Yellowish brown
260 . . .	Light brownish purple
270 . . .	Reddish brown
280 . . .	Purple
290 . . .	Dark purple
300 . . .	Blue
310 . . .	Dark blue
320 . . .	Greenish blue
330 . . .	Greyish blue
340 . . .	Steel grey
350 . . .	Light brownish grey
360 . . .	Brownish grey

half an hour at a temperature of 200°C. to 400°C. The treatment may be repeated two or three times to obtain a good finish. By the introduction of sulphur into the oil, darker shades of colour can be produced. Another method consists in heating the metal for $1\frac{1}{2}$ to 2 hours at 650°C. in a carburising compound or in a smoky atmosphere. The process of barrelling in charred sawdust to obtain a black finish has also been employed.

Very tenacious oxide coatings can be formed on iron and steel by subjecting the metal to heat in alternate oxidising and reducing atmospheres.

Bower-Barff Process. In the Bower-Barff process, the steel is heated to about 800°C. for twenty minutes, first in contact with air, and then in superheated steam. A coating consisting of a mixture of Fe_2O_3 and Fe_3O_4 is formed, after which heating is continued in a producer-gas atmosphere which converts it entirely to Fe_3O_4 . This coating is said to have high durability owing to the fact that both the underlying metal and the oxide have similar coefficients of expansion.

Another process makes use of low-pressure steam, partially dissociated by being passed through a hot iron tube. The metal is heated in this atmosphere at about 600°C. for half an hour, after which it is heated in the presence of oil fumes for a further fifteen minutes.

The methods described above are capable of giving finishes of good appearance and durability if carefully carried out. They are regarded, however, as essentially craftsmen's processes and are not readily suited to factory production, where speed and uniformity are required. They are now used in industry to a relatively limited extent.

Black Oxide Finishes. A simplified procedure for heat bronzing has therefore become increasingly popular in recent years, and consists in immersing the metal in molten sodium nitrate maintained at a temperature of about 300°C. Sometimes a mixture of sodium and potassium nitrates is employed, as this has a lower melting-point than either salt alone. This method gives a greater speed and uniformity of heating and pleasing blue-black colours can be obtained. Brown colours require a lower temperature and rather more skill to produce. A common procedure is to heat the parts in sand at a temperature of 240°C. to 260°C. These processes are also being largely superseded by caustic alkali-nitrate methods.

Caustic Alkali-Nitrate Processes.—Amongst the most widely used black oxide finishes are those produced by immersion in caustic

alkali solutions containing an oxidising agent, generally a nitrate. There are a number of proprietary processes commercially in use nowadays based essentially on this principle, although some of them incorporate special additions of activating agents to the alkali-oxidising agent mixture which, it is claimed, give good results and increase the life of the bath. The baths are liable to deteriorate with use, due to the accumulation of iron salts, so that their action is retarded. The activators may be selected from the group of compounds which form complexes with the iron salts (e.g. cyanides, tannates, and tartrates).

Typical solutions of this kind can be made up by dissolving 120 to 150 gm. of caustic soda in about 100 c.c. of water, and adding about 30 gm. of sodium nitrate. The concentrated solution thus produced is used at its boiling-point, which is high. The temperatures are of the order of 280 F. to 300 F., depending on the concentration of salts. The steel parts are cleaned and immersed for a period of five to thirty minutes in the solution until a satisfactory colour is obtained. The coatings thus formed may be as much as 0.001 to 0.002 in. in thickness. A formula given by Harris⁽³⁾ is as follows:

Caustic soda	80 oz.
Potassium nitrate	50 oz.
Water	1 gallon
Temperature	140°C.
Time	10 minutes

As evaporation of water takes place, the concentration increases so that the boiling-point rises; more water must therefore be added from time to time to maintain a constant boiling-point, this being useful as a measure of the strength of the solution. Addition of water must be carried out with circumspection, as the solution is liable to splash when the water is introduced. Sometimes a small amount of nitrite is added to the bath, but this does not appear to be of great value. Heating of the solution, which is used in a cast-iron or steel tank, must be very uniform. When gas is employed, the heat should be directed on to the sides as well as on to the bottom of the steel tank by suitable baffles to prevent stratification of the very dense solution and to maintain it gently at the boil.

These solutions also deteriorate with use, due to the absorption of carbon dioxide which converts the caustic soda into the less effective sodium carbonate. Other oxidising agents, such as potassium permanganate or sodium dichromate, have been used either

together with or in place of sodium nitrate. It is common practice to use two baths for immersion, the first being kept at a lower concentration (and hence at a lower temperature) than the second. The articles are immersed for a short time in the less concentrated bath prior to treatment in the second main tank. This procedure gives a somewhat better coating.

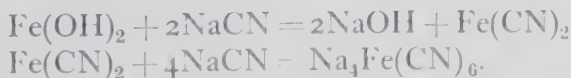
Additives.—Krause⁽⁴⁾ recommends the use of urea in alkali-nitrate solutions. With an admixture of 20 gm. per litre of urea to a caustic soda solution containing 10 gm. per litre of sodium nitrate, it is stated that iron was coloured a deep dull black and steel a glossy black in twenty to thirty minutes at 260° F. At 280° F. the colours were produced in five minutes.

In the "Jetal" process,⁽⁷⁾ which has been extensively employed in the U.S.A. for black finishes of this description, a bath is made up of the following composition:

Sodium hydroxide	.	3 lb.
Sodium nitrate	.	1 lb.
Water	.	4 lb.

This is operated within a temperature range of 250° F. to 300° F., an optimum temperature of 275° F. to 290° F. being preferred. The time of treatment may be up to thirty minutes, depending on the colour and the depth of coating required.

After the bath has been in use for some time it will be found that it has become exhausted so that only a poor coloration or no colour at all is produced. It should be possible to treat about 30 sq. ft. of surface in 1 gallon of solution before this stage is reached. When the bath begins to lose its efficiency about $\frac{1}{2}$ lb. of sodium cyanide is added per 100 lb. of bath, and, if necessary, some caustic soda and more nitrate to replace "drag-out" losses. This regenerating treatment is repeated as needed, an addition of about $\frac{1}{2}$ lb. of sodium cyanide being required for each 100 sq. ft. of metal treated. The cyanide probably serves to remove excess iron ions from the solution by the formation of sodium ferrocyanide, $\text{Na}_4\text{Fe}(\text{CN})_6$, so that the iron goes into the anionic complex, the reactions which occur being represented thus:



The initiation of the reaction is sometimes slow, so that blackening does not readily occur; this is particularly the case with cast iron and

sometimes with cold-rolled steel sheet. It has been recommended that the metal be immersed for some minutes in a 5 to 10 per cent solution of hydrofluoric acid prior to treatment to expedite the reaction in such cases.

Characteristics of Black Oxide Coatings.—As has already been mentioned, chemical blackening processes are more readily carried out than heat bluing or browning, while the methods are better adapted to factory production. For parts which are kept oiled and cleaned they are useful, but the corrosion resistance of the finishes under conditions of exposure is very low indeed, and is largely ascribable to the oil film with which the oxide coating is generally impregnated. The oxide has not a great deal of absorptive capacity for oil in any case, so that the oil must be constantly renewed or it will be readily removed and rusting will occur. The oxide coatings are, however, fairly hard and will resist a considerable amount of mechanical wear.

These treatments have also been employed to aid the adhesion of paints and lacquers, and to minimise the spread of corrosion should a break in the organic coating manifest itself. Again, owing to the relatively poor absorptive characteristics of the oxide coat, its usefulness in this direction is not as great as is that of the phosphate coatings (*vide infra*). Fig. 49 shows the appearance of black oxide coated and oiled steel components as compared with some which have been phosphatised, stained and oiled, after twenty-four hours' salt spray test.

The alkali-oxidising agent method is unsuited to the treatment of assembled parts containing folds, recesses, or soldered joints. The reason is that the highly hygroscopic salts accumulate within the joints; subsequently corrosion is likely to occur, due to the seepage of the salts and consequent corrosive attack on the metal surface. After-treatment (e.g. immersion in weak acids to remove retained alkali on parts of this type) is often resorted to, but the efficacy of such means is very doubtful, the alkali being usually partly replaced by a no less harmful neutral salt. These finishes are, therefore, best avoided where there are recesses or crevices liable to retain salts.

Blue Finishes.—Blue finishes on steel are highly popular and can be produced by chemical methods. One type of solution which is often employed consists of 20 oz. of sodium thiosulphate and 7 oz. of lead acetate dissolved in 1 gallon of water. The solution is maintained at a temperature of about 180 F., the treatment time being around five minutes.

An alternative process consists in immersing the parts in a boiling bath containing 1 oz. per gallon each of potassium ferrocyanide and ferric chloride.

Stainless Steel.—Stainless steel is exceedingly difficult to colour because of the protective oxide which normally is present on the steel, and gives it its corrosion-resisting properties. It is, however, possible to produce a durable black coating by immersion in molten

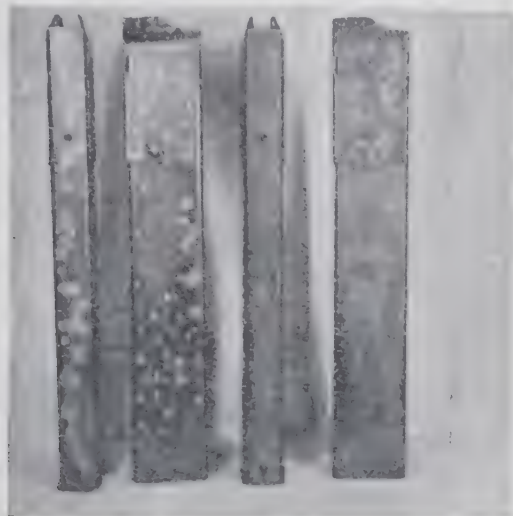


Fig. 40.—Gun magazines after twenty-four hours' exposure to salt spray. Left-hand pair, alkali-nitrate black finish, oiled. Right-hand pair, phosphate-coated, black stained and oiled

sodium dichromate at a temperature of 730° F. to 750° F. The treatment time is 20 to 30 minutes, after which the work is allowed to cool and rinsed in hot water.

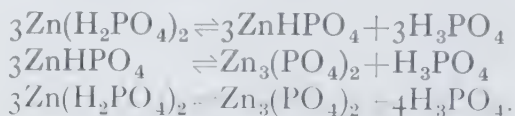
PHOSPHATE COATINGS

Since their original development by Coslett in 1906⁽⁶⁾ phosphate coatings have been increasingly used in the protection of ferrous metals where a very high degree of rust-resistance is not required. Several types of phosphate coating processes are now available as a result of the considerable amount of research which has gone into their development and application.

Phosphate coatings are applied to metals by treating them in dilute aqueous solutions containing phosphoric acid and one or more of the primary phosphates of iron, manganese, or zinc with or without the addition of materials acting as accelerators.

Treatment is carried out by dipping or spraying after careful cleaning of the metal surface, the time of treatment depending on the solution used, the coating thickness required and the operating temperature. After treatment the metal is rinsed and is often given a passivating dip in a chromic acid or chromate solution, dried and impregnated with an oil or other protective medium.

The phosphating solution reaches a state of equilibrium which depends on its temperature and the relative concentrations of the chemicals present. Primary iron, manganese or zinc phosphates dissociate to form secondary or tertiary phosphates. Zinc phosphate, for example, dissociates as follows:



With the exception of the secondary zinc phosphate the salts produced are only slightly soluble, and in the absence of free phosphoric acid are precipitated as sludge by any factor which causes increased dissociation, e.g. rise in temperature or increased dilution. Free phosphoric acid must therefore be present to drive the reaction to the left. When a ferrous metal is immersed in the bath the iron dissolves and hydrogen ions are discharged. The reduction in hydrogen ion concentration in the solution layer adjacent to the metal therefore causes the equilibrium to shift to the right with the result that the solubility products of the secondary and tertiary phosphates are exceeded locally, and these salts precipitate from the solution at the metal surface and the phosphate coating forms. Restoration of the original state of equilibrium takes place, partially at any rate, by the action of the phosphoric acid which is formed.

Coslett's Process.—Coslett's original solution was prepared by dissolving iron filings in phosphoric acid and immersing the ferrous articles to be treated in the solution, which was kept as near to the boiling-point as possible. It consists essentially of an aqueous solution of phosphoric acid saturated with ferrous phosphate.

Phosphoric acid, H_3PO_4 , forms three series of salts, being a tribasic acid. The primary metal phosphates of the heavy metals in which one of the hydrogen atoms is replaced are generally readily soluble in water, the secondary phosphates are less soluble, while the tertiary phosphates, containing no replaceable hydrogen, are practically insoluble. The method of treatment consists in immersing the articles in the solution until the evolution of hydrogen has ceased; the reaction is then complete and a coating, consisting in the main

of the insoluble tertiary phosphate, is formed on the metal surface. This may take as long as three to four hours, depending on the type of metal which is being treated. Small parts may be handled in a slowly rotating perforated barrel immersed in the heated solution; when the treatment is finished, the parts are rinsed and dried off.

Apart from the prolonged treatment times needed to produce satisfactory coatings in Coslett's iron solution, it was also found that it tended to oxidise rapidly with the precipitation of the phosphates in the form of insoluble ferric phosphate, which was thrown out in the form of sludge, thereby reducing the efficiency of the process.

Coslett's Zinc Solution.—The next development was the adoption by Coslett of a solution of zinc phosphate in phosphoric acid, and this process became known as "Zinc Coslettising". The procedure was to make up a solution by dissolving 290 gm. of zinc in a 50 per cent solution of phosphoric acid to form a paste. This paste was then dissolved in water to the extent of 1.5 to 2 per cent, and the resulting solution used boiling, the time of treatment being about two hours.

Coslett's zinc solution works better when it has been in use for some time, due to the formation of iron phosphate in the solution, and Coslett's patent stipulated the use of iron phosphate with the zinc. The usual concentration of free acid is in the neighbourhood of 2.5 to 3 per cent and the best protection is said to be obtained when the ratio of phosphate to free acid is kept at about 7 or 8 to 1. If the acid content is too high the time of treatment will be prolonged, while too low an acid content will result in the formation of a loose crystalline deposit and also in the precipitation of residues in the bath.

The acid zinc solutions are, however, capable of retaining in solution the higher ferrous phosphates (which are produced by interaction with the iron). The bath therefore becomes progressively loaded with soluble phosphates, so that it begins to lose efficiency. By the introduction of small proportions of mild oxidising agents, the basic ferrous phosphates are gradually oxidised to the ferric state, and as these salts are practically insoluble, they are precipitated and the life of the solution is correspondingly increased. The coatings consist primarily of tertiary zinc phosphate with small amounts of secondary and tertiary iron phosphate. The use of modified zinc processes of this type is now extensive, the two best known being "Bonderizing" and "Granodizing". These addition agents are termed "accelerators".

Accelerators.—The accelerators which are employed probably

function by oxidising the hydrogen evolved at the metal surface. Strong oxidising agents are, however, unsuitable as ingredients of the phosphatising bath, since they convert any ferrous phosphate to the ferric state, immediately disturbing the balance of the solution and thus impairing the functioning of the bath. Suitable oxidising accelerators are materials such as alkali metal nitrates (e.g. sodium nitrate), nitrites, copper salts, and chlorates.

When nitrites are used they must be added in the form of a "toner" from time to time, since excessively rapid decomposition would occur if the nitrites were introduced in bulk, and an adequate concentration could not be maintained. The concentration of the accelerator in relation to the concentration of iron salts and free acid in the bath plays an important part in the type of coating obtained and its thickness.

By the use of accelerators the time of treatment can be reduced from an hour or more to ten minutes or less. Increasing the concentration of oxidising agent reduces the amount of gas evolution progressively, and hence the time for the formation of the coating. There is, however, an optimum concentration, and if more accelerator is added the phosphate layer may become coarse and streaky. By increasing the free phosphoric acid, however, good coatings can again be obtained. This effect has been noted by Machu⁽⁷⁾, who points out that excessive concentrations of oxidising agents cause the surface to become passive, but that this can be counteracted by increasing the concentration of free phosphoric acid.

Copper salts act as accelerators by increasing the rate of dissolution of iron. The copper is deposited in small particles on the steel surface so that numerous minute electro-chemical cells are formed which accelerate the formation of the coating. The presence of copper in the finished surface has an adverse effect on its protective value, however, so that this type of accelerator is tending to be superseded.

A more recent development makes use of the so-called "nitro-accelerators",⁽⁸⁾ of which typical examples are the nitro-derivatives of aliphatic compounds, e.g. nitro-urea, nitroguanidine, and nitro-urethane and nitro-derivatives of aromatic compounds, e.g. nitro-benzene, the nitro-benzoic acids, and picric acid. Organic and inorganic cyanides, sodium nitroprusside, and hydroxylamine have also been proposed as accelerators. Nitroguanidine is claimed to be not only an accelerator of the reaction, but also a stabiliser of the zinc acid phosphate. It must be intimately mixed with the phosphate to the extent of 5 to 15 per cent.

In the presence of accelerators the phosphating process is completed rapidly, although the reaction continues for some time after

the end of hydrogen evolution (unlike the non-accelerated baths). The first function of the accelerator is probably to increase the number of local cathodic areas on the metal surface in relation to the anodic areas. Since it is at these local cathodes that hydrogen ions are discharged and the phosphates precipitated, any process which will increase the number of such centres will accelerate the reaction. The mechanism by which this result is achieved varies. Oxidising agents appear to render anodic areas passive in some cases whilst in others the local precipitation of cathodic constituents may be the effective action.

The addition of accelerators to phosphatising solutions is now common practice, but more recently it has been found that improved results can be obtained by increasing the concentration of accelerator actually at the metal surface. This is done by applying the accelerator before the coating solution.⁽⁹⁾ In practice, the surface to be treated is dipped into or sprayed with a solution of the accelerator, after which the coating solution is applied by a dipping or spraying operation. The accelerators which have been found especially suitable are sodium or potassium nitrate and the organic nitro-accelerators mentioned above. The metal surface is first cleaned thoroughly and then immersed in or sprayed with the accelerator, consisting of a hot solution of up to about 0.5 to 1 per cent concentration of the activating material. The metal is then immersed directly into the phosphate bath. In this way a small amount of accelerator is introduced continuously into the main phosphatising solution by drag-out from the previous treatment tank. This has a further advantage, inasmuch as if accelerators, such as nitrites, for example, are put directly into the phosphate solution in any considerable concentration, they tend to be decomposed before actually coming into contact with the metal being treated. By the method described the accelerator concentration in the phosphate bath is maintained at about 0.002 per cent.

Sludge.—All phosphating baths tend to form sludge continuously during their operation, and this sludge may be deposited on the work, causing uneven coatings which interfere with subsequent finishing operations, especially painting. The sludge in the commonly used zinc solution consists almost entirely of tertiary zinc and iron phosphates. The use of oxidising accelerators in theory increases sludge formation by virtue of the fact that they oxidise the soluble ferrous ions to the insoluble ferric salt. In actual practice, however, this is not the case, since the coating forms so much more rapidly than in the absence of an accelerator.

Commercial Processes. —The well-known "Parkerizing" treatment makes use of a solution of acid manganese phosphate for the treatment of ferrous metals. It was found that this solution will produce a satisfactory phosphate film on steel in a considerably shorter time than Coslett's iron solution. For the treatment of steel and some non-ferrous metals prior to painting the zinc phosphate processes are preferred because of the fine and smooth coatings produced by them. These make use of acid zinc phosphate solutions containing various accelerators. The best-known commercial variants of these processes are Bonderizing and Granodizing. The use of manganese phosphates has the advantage that they have rather less tendency to oxidise and form insoluble sludges, so that the primary acid phosphate concentration of the bath is maintained. The solutions are used at or near the boiling-point, the time of treatment being about an hour, during which time a coating of some 0.0003 in. to 0.0005 in. in thickness is produced. Regular additions of the acid phosphate must be made to maintain the correct acidity, and if the tank is cleaned from time to time to remove the sludge which settles to the bottom, the solution can be used almost indefinitely.

Under these conditions both iron and manganese solutions precipitate coatings of secondary and tertiary phosphates on the metal surface. The manganese phosphates are superior from the protective point of view to the secondary and tertiary ferrous phosphates as the latter are oxidised by the air gradually to the ferric state. The change in the crystalline form resulting from this leads to lack of adhesion of the coating and increased crystal size with consequently greater permeability to air and moisture; the protective value is therefore considerably reduced.

As the phosphate is removed from the solution by the reaction it must be replaced by the addition of more primary acid phosphate. The commercially available salts manufactured for phosphate treatment often consist of complexes containing more phosphoric acid than is required by the formula of the primary acid phosphate so that the acidity of the bath is maintained without specific addition of free phosphoric acid.

For satisfactory phosphatising the concentrations of the metal, hydrogen and acid phosphate ions must be such as to ensure that deposition of insoluble phosphates will be confined as far as possible to the liquid-metal interface. This can only be achieved if the solubility products of the secondary and tertiary phosphates are high but are not exceeded. When an iron surface is then immersed in such a solution the hydrogen ion concentration at the interface

is reduced by the liberation of hydrogen and secondary and tertiary phosphates of the metal are precipitated locally. More hydrogen ions are again liberated to restore equilibrium in the bath and the process is then repeated.

Control.—The ratio of combined to free phosphoric acid in the solution is important if satisfactory results are to be obtained. It is essential to maintain as high a proportion of the insoluble tertiary phosphate in the coating as possible, to keep the treatment time to a minimum, and also to maintain a phosphate film of fine crystal structure. All these are favoured by a low proportion of free phosphoric acid. Too low a ratio is, however, equally undesirable as it leads to excessive hydrolysis with the result that the insoluble phosphates are precipitated in the body of the solution. This is wasteful of chemicals and undesirable in other respects. A ratio of about 7 or 8 to 1 of combined to free phosphoric acid gives a good coating in a reasonable processing time.

The total concentration in the bath is determined by titration with caustic soda solution using phenolphthalein as indicator, and must also be carefully controlled, although it has little influence on the combined free phosphoric acid ratio. A concentration of 2.5 to 3 per cent is common. The "free acid" concentration can be determined by titration with methyl orange as the indicator; Macchia has suggested that a better end-point is obtained if bromophenol blue is used.⁽¹⁰⁾

In the case of a zinc phosphate bath containing an accelerator decrease in the acid ratio (excessive free acid) causes a progressive darkening of the coating and the formation of large sparkling crystals. It is found that the latter contain increasing quantities of iron phosphates which are formed as a result of the etching action of the more concentrated solutions. Simultaneously the protective value of the coating decreases as it becomes darker or more crystalline.

The change in weight of the metal being treated is determined by the relative amounts of iron dissolved and phosphates precipitated. As the acid ratio decreases so does the loss in weight.

The total concentration of chemicals in the bath is of considerable importance. At low total concentrations precipitation of secondary and tertiary phosphates takes place not only at the metal surface but rapidly throughout the bath, causing sludge formation and waste of materials. Conversely, excessive absolute concentrations may cause excessive etching of the metal being treated and the equilibrium change will be delayed. The acid produced when precipitation takes place tends to re-establish equilibrium, and it may also dissolve the

coating. In the case of baths of high or low absolute concentrations the treatment time is prolonged and sludge formation is high, whilst the corrosion resistance of the coatings is also adversely affected.

Method of Operation. Modern phosphatising processes are simple to operate and the solutions are prepared by dissolving the appropriate chemicals in water, boiling for about an hour and commencing treatment immediately. The acid phosphates are commercially available as proprietary compounds containing the necessary activators. The crystalline iron and manganese acid orthophosphates are the most commonly used materials, and these are to be preferred to solutions containing excess phosphoric acid, since the presence of the latter acid in the solution has a detrimental effect on the durability of the coating produced. Owing to its hygroscopic nature, the zinc acid phosphate mixtures are generally supplied in the form of a concentrated aqueous solution, and this is diluted and employed for treatment as required.

The metal to be treated is immersed in the solution, or, alternatively, the phosphate solution can be sprayed on to the surface. The time of treatment varies with the composition and temperature of the solution and with the thickness of coating required. The use of an accelerator tremendously reduces the time required to produce a coating of a given thickness. The quality of the coating produced is judged by its colour, smoothness and uniformity, adhesion, crystal size and corrosion resistance. High working temperatures of the bath favour the rapid formation of uniform coatings, but at the same time increase the rate of sludge formation. At lower temperature coarse and uneven coatings tend to be produced which have inferior corrosion resistance.

The concentration of the phosphating bath is important, there being definite optimum concentrations. In the case of zinc phosphate solutions these are:

Primary zinc phosphate	.	.	.	1.5 to 3 g./l.
Phosphoric acid	.	.	.	3 to 4 g./l.
Accelerator	.	.	.	3 to 4 g./l.

The smoothness of the coatings improves as the concentration becomes lower within the above range. The concentration of the oxidising accelerator is important, since if it is inadequate in amount the hydrogen liberated will cause poor coatings, whilst too much accelerator will give rise to the formation of streaked and uneven coatings.

Preparation of the Phosphates. The dihydrogen orthophosphates

of the metals are commercially prepared by dissolving them in a hot concentrated solution of orthophosphoric acid (60 to 75 per cent strength) to form a soluble phosphate, cooling the solution, and then crystallising out the salt which is removed from the mother liquor by centrifuging.⁽¹¹⁾ Ferrous dihydrogen phosphate, $\text{Fe}(\text{H}_2\text{PO}_4)_2$, is likewise made in this way, whilst the manganese and zinc salts ($\text{Mn}(\text{H}_2\text{PO}_4)_2$ and $\text{Zn}(\text{H}_2\text{PO}_4)_2$ respectively) may be produced similarly. The zinc salt melts at 60° C. so that care must be taken to avoid overheating the crystals in the course of manufacture.

Iron dissolves with difficulty in phosphoric acid, so that the phosphate solution is not easily prepared. Ferrous sulphide dissolves much more easily and in the *Walterisation process*⁽¹²⁾ advantage is taken of this fact in order to prepare iron phosphate solutions more readily. Otherwise the Walter process is very similar to the Coslett iron process.

Nowadays, the iron and manganese salts are produced together from ferro-manganese, which is a readily available material produced from the ore and containing some 80 per cent of manganese, 6 to 10 per cent of iron, the rest being impurities of various kinds. By dissolving the ferro-manganese in a 65 per cent solution of phosphoric acid, the iron and manganese salts are formed, and by drying the resulting crystals by centrifuging, the ferrous salt is oxidised to the insoluble ferric phosphate. On re-dissolving, the manganese salt is left in solution, since the latter does not readily oxidise. In this way, by filtering prior to re-crystallisation the manganese salt is obtained in a practically pure form.⁽¹³⁾ In actual use iron dissolving in the manganese phosphate bath results in the formation of acid iron phosphate in the solution, and the coating consists of a mixture of both the iron and manganese phosphates. The best coating should contain at least one-half as much manganese again as iron, and for this purpose the bath should contain at least one-third as much manganese dihydrogen phosphate as it contains ferrous dihydrogen phosphate.

Composition of the Coat.—The proportion of manganese in a coating is generally higher than that present in the treatment solution. Some of the iron dissolved in the bath forms insoluble phosphates which are deposited as sludge and part of it remains as ferrous dihydrogen phosphate dissolved in the bath. As the bath is used it becomes less rich in manganese and richer in iron (dissolved in the form of dihydrogen phosphate). The manganese content of the bath is determined by its acidity as measured by the amount of alkali required to neutralise a given amount of solution, using

phenolphthalein as indicator. The appearance of typical phosphate coatings can be seen from the photomicrograph (Fig. 50).

Effect of Temperature.—The temperature of treatment is important since it is desirable to produce a phosphate of small crystal size. Coatings of large grain size, such as are formed when the temperature

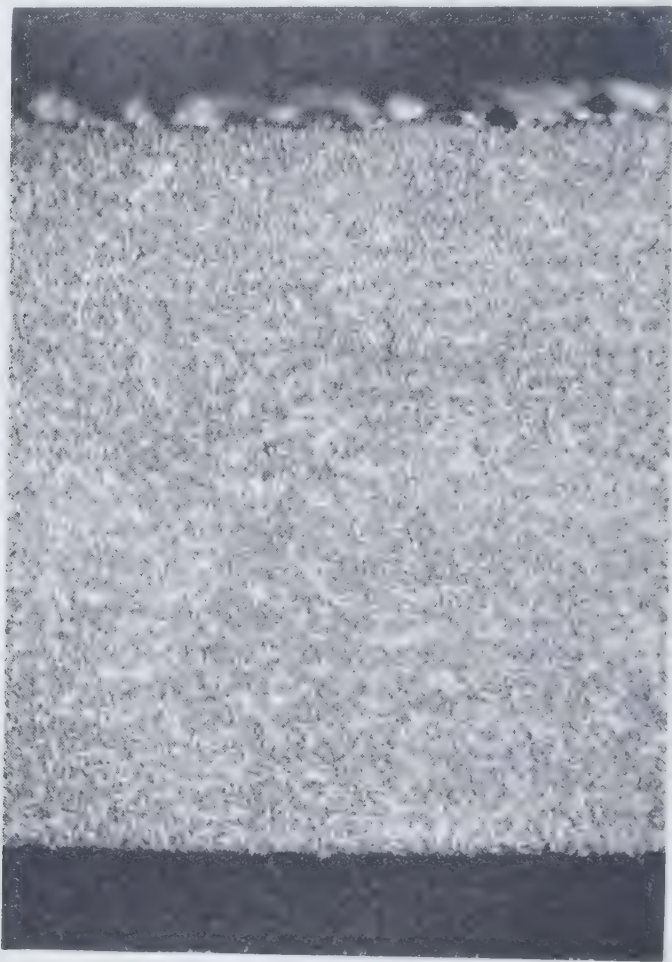


Fig. 50.—Bonderized mild steel surface ($\times 25$)

of treatment is reduced, have poor corrosion resistance. Thus Macchia⁽¹⁴⁾ has determined the resistance to rusting in a 3 per cent sodium chloride solution of steel treated in a 3 per cent solution of manganese dihydrogen phosphate; the results are shown in Fig. 51. It is seen that as the temperature falls from 98° C. to about 80° C. the corrosion resistance is reduced by half. Macchia also found that the treatment time increased correspondingly. Thus, at 98° C. the time taken was ten minutes; at 88° C. the time was increased to forty

minutes; whilst at a temperature of 70°C . the reaction was incomplete even at the end of three hours.

It has also been established recently that the rate of formation of the phosphate coating can be increased by bringing the solution into contact with the metal surface by pressure, such as can be applied by rubber rollers. This method is particularly applicable to the treatment of sheet, and the process time can be reduced to three to ten seconds. Brushes can also be employed for this purpose. Besides accelerating the rate of formation of the coating, the use of brushes or rollers tends to make the phosphate layer more fibrous in structure and so able to withstand deformation. It has, in fact, been claimed

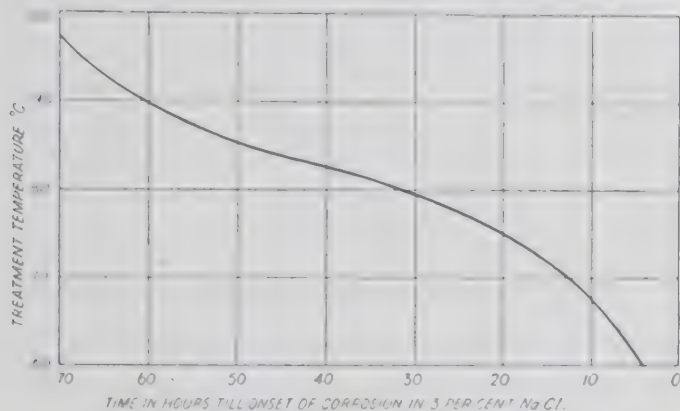


Fig. 51. —Influence of treatment temperature on corrosion resistance of steel phosphate-coated in 3 per cent manganese dihydrogen phosphate solution

that sheet phosphated in this way and painted can be fabricated after painting without injury to the coating.⁽¹⁵⁾

Cleaning.—In applying phosphate coatings to steel the pre-cleaning of the metal is important. A common procedure is to degrease the parts in trichlorethylene, whilst, if the metal be at all rusted or scaled, barrel cleaning may be successfully employed. Rust must be carefully removed, since although some phosphate solutions, such as those containing copper salts as accelerators, will treat slightly rusted articles, others (notably the zinc solutions) are very unsatisfactory where rust is present. In any event, coatings on rusted metal are apt to have a lower durability than those produced on clean steel. Pickling or cleaning in strong alkalis, or, in fact, any process in which the metal is subjected to the action of powerful electrolytes, is to be avoided. The reason is that such materials appear to activate the grain boundaries of the metal in such a way that the phosphates are irregularly formed. A rough and granular coating of large grain size,

which has poor protective qualities, then results. Mild alkalis can be used successfully, however. Very thorough rinsing is essential after cleaning to avoid contamination of the phosphate bath.

The coarsening effect of pickling on the grain size of the phosphate coating can be seen in Fig. 52. The left-hand photograph shows the coating obtained on a steel surface degreased by solvent only; the right-hand illustration shows the large grained coating produced when the same steel surface was acid pickled.

These photographs were produced by the replica technique. The



Fig. 52.—Effect of surface treatment on phosphate coating

phosphated surface is moistened with a suitable solvent, after which a cellulose acetate tape is pressed on to the area to be examined. The tape is allowed to dry and removed, when a perfect replica of the crystal structure is obtained which can be examined by transmitted light or photographed. In this way a much clearer picture of the structure of the coating can be obtained than when the examination is carried out by the reflected light method.

Impregnation. Phosphate coatings sometimes tend to be powdery on the surface, and they have relatively little corrosion resistance when used alone. To be of maximum value the film must be impregnated, the commonest treatment being to stain it black in a boiling solution of a dye (e.g. nigrosine) to improve its appearance, and to

immerse in hot oil. Linseed oil or a mineral oil may be employed. On removing from the oil bath and wiping or centrifuging off excess oil, a pleasing finish is obtained, which is extensively employed on small parts such as nuts, washers, bolts and springs, and on components operating in the presence of oil or where conditions of exposure are not unduly severe. Recently it has been found that oil films applied by immersion of the articles in hot concentrated aqueous emulsions of the oils followed by drying are capable of giving exceptionally good protection. Phosphatised coatings of this description

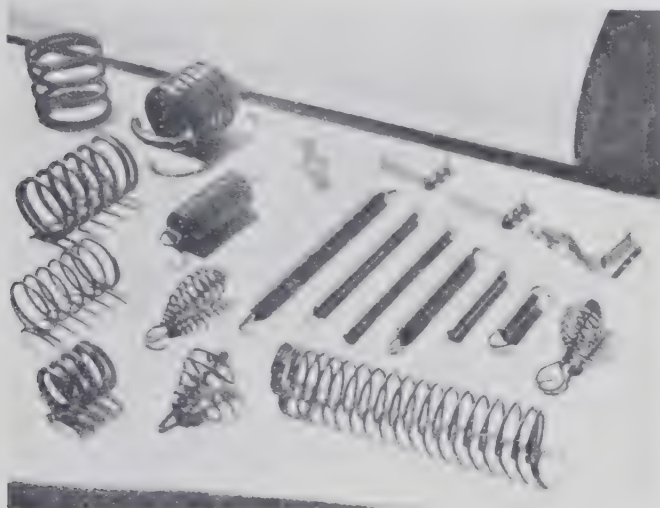


Fig. 53.—Some examples of phosphatised springs

can give very satisfactory service, although they do not withstand abrasion or wear too well on account of their intrinsic softness. This type of finish is very useful for springs because the tendency for hydrogen embrittlement to occur is less than is the case with plated finishes (Fig. 53). A rinse in a weak chromic acid solution (about 0.05 per cent) prior to impregnation markedly improves the protective value of phosphate coatings, and this is now common usage.

The above treatment is usually applied to the manganese phosphate type of coating, which is thicker and rather more absorbent than that produced by the zinc processes. The coatings can also be impregnated with solutions of waxes or with dilute lacquer solutions (e.g. plasticised shellac lacquers), and in this way satisfactory finishes can be obtained which are suitable for conditions of service where an oil film may be a disadvantage.

Pre-treatment for Painting.—As a basis for the application of paints and lacquers, however, the zinc phosphate processes are to be preferred to the manganese phosphate coatings. Besides being much more quickly applied, they are thinner and less granular in nature, so that a smooth paint film is more readily obtained. The adhesion of paint to steel pre-treated in this way is much better

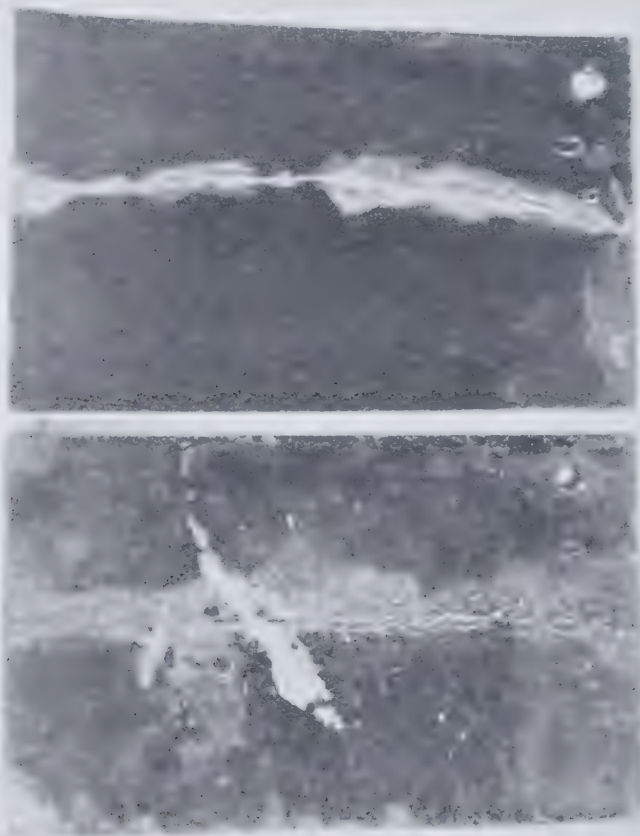


Fig. 54. —(Upper) Steel sheet phosphatised and black spray-painted. After scoring and exposure for six months. (Lower) Similar sheet with phosphate treatment omitted

than on bare steel, while the lateral spreading of rust areas under any breaks that may occur in the paint film is slower on pre-treated surfaces (Fig. 54). The effectiveness of phosphate coatings as an undercoat for paint is based on their large specific area and high porosity which cause better wetting and adsorption of the paint to take place. Improved mechanical adhesion also results from the crystalline nature of the coating, even when it is very thin. Phosphatising is also useful, in that it nullifies the possible ill-effects of

traces of corrosive acids which might be left in the pores of the metal if it has been subjected to acid pickling at any stage.

The insoluble nature of the phosphate coatings often make these finishes suitable for the treatment of complex metal parts or riveted assemblies containing recesses or joints. Many finishing processes, notably electro-plating and the caustic alkali blackening processes already described, cannot be used on such assemblies owing to the danger of chemicals being retained in folds or recesses and seeping out during subsequent service.

Spray-Phosphatising.—As a basis for painting, zinc phosphate processes are extensively employed in the spray-type of plant. Here the hot solution is sprayed under pressure on to the parts to be treated as they pass through the plant on a chain conveyor. From the point of view of speed of operation and economy of space and materials spray-phosphatising methods have much to commend them, and they provide a suitable base for subsequent painting; the coatings are, however, neither as uniform nor as effective as those produced by immersion methods. In spite of the ingenuity which has been exercised in the design and location of spray jets, it is almost impossible to ensure that the flow of solution will reach every part of a complex-shaped article for an adequate time to produce a good coating at all points on its surface.

Electro-Granodine.—Thick phosphate coatings can be built up more rapidly by the use of electric current in conjunction with the phosphate solutions. In the Electro-Granodine process⁽¹⁶⁾ the parts are suspended in the hot acid phosphate solution and an alternating current at a pressure of about 20 volts is applied. In about three minutes a resistant coating approximating 0.0005 in. thick can be built up and after rinsing and drying, the parts may be stained and oiled or painted. Electrolytically produced phosphate coatings appear to have rather better durability than those formed by immersion methods, but the plant required is rather more complicated.

Cold Process Phosphate Treatment.—Much investigation has been carried out in an endeavour to develop a rapid phosphatising process which will operate in the cold. By a "cold" process is meant one which will operate without the need for artificial heating. This may mean temperatures of up to 120°F., since articles are often warm when put into the solution, and this, coupled with the development of a certain amount of heat as a result of the chemical reaction, will serve to maintain the solution at temperatures of this order.

The elimination of heating coils, especially in the spray-type of plant, is a great advantage. The reason is that scale tends to deposit

rapidly on steam coils, so that they become covered with an insulating coating which is very difficult to remove and slows down the rate of heat transfer very considerably. Some improvement in reducing the tenacity with which the scale adheres to the heating coils can be effected by heavily nickel-plating them or by treating them with special paints, but these measures are only palliatives and are not wholly effective. The local heating also causes the precipitation of zinc phosphate and the loss of zinc from the solution.

At low temperatures such sludge as is produced in the reaction is lighter in texture and is non-adherent. It does not, therefore, accumulate in nozzles and pipes of spraying plant, and thus eliminates the need for chipping and hammering to remove scale accumulations. The sludge can be washed away very largely when necessary by flushing with water.

One cold process makes use of a solution of acid zinc phosphate containing hydrogen peroxide (or a compound capable of forming hydrogen peroxide in solution, such as sodium percarbonate or perborate), with additions of an alkali such as sodium hydroxide or sodium carbonate from time to time.⁽¹⁷⁾ The object of the alkali is to neutralise the free phosphoric acid produced by the hydrolysis of the zinc phosphate in solution, and also as a result of the oxidation of any ferrous phosphate and its subsequent precipitation as ferric phosphate. The alkali is also used to keep the solution in a condition slightly supersaturated with respect to zinc phosphate; this can be achieved by maintaining a pH of more than 0.1 above the pH at equilibrium of the solution. The zinc content of the solution is kept between 1 and 5 gm. per litre with a hydrogen peroxide concentration of 0.04 to 0.24 gm. per litre.

A cold phosphate process described by Földes⁽¹⁸⁾ consists of a zinc solution containing sodium nitrite and fluoride. The pH of the solution must be kept within defined limits for satisfactory results. As has already been pointed out, the lowered rate of coating formation at low temperatures cannot be counteracted by increasing the free acid concentration, and it has, in fact, been shown that the amount of free acid required to keep tertiary zinc phosphate in solution at low temperatures is very considerably less than that required at the boiling-point. Fluorine compounds are useful in maintaining pH constancy in this type of bath, and a low free acid concentration is necessary.

Phosphatised Zinc Coatings.—Zinc can be phosphate treated successfully, and a phosphated electro-galvanised coating has been proposed to give a very durable undercoat for paint where higher

resistance to corrosion is required than is obtainable by direct phosphate treatment on steel. In this process,⁽¹⁹⁾ the ferrous metal base is plated with a very thin zinc coating, of the order of 0.00001 to 0.00003 in. thick, in any case not exceeding 0.0001 in. It is then phosphate treated so that part of the coating is converted to insoluble phosphate. A suitable procedure is to immerse for fifteen seconds in a normal acid zinc phosphate solution working at a temperature of about 135° F. In this time about half of the zinc coating will be converted to a phosphate coating of small crystal size which provides a good undercoat for paint and will not interfere with spot welding. In this way finishes of high durability can be obtained, and the method is already in large-scale use, especially in the U.S.A. Subsequently, the phosphate film can be further improved by immersion in a chromic acid solution containing 2 gm. per gallon of water applied for ten to twenty seconds, at a temperature of about 175° F.

It is worthy of note that, by wiping a zinc surface mechanically prior to phosphatising, the crystalline structure of the coating becomes greatly refined and the corrosion-resistance is consequently improved.⁽²⁰⁾ The reason for this phenomenon is not clear, but it may be due to changes in adsorbed surface layers on the zinc.

Titanium Pre-Dip.—More recently, Jernstedt⁽²¹⁾ investigated a series of solutions with a view of obtaining a pre-dip treatment which would increase the corrosion-resistance of a phosphate coating. It was found that immersion of zinc-coated or plain steel in a 1 per cent solution of disodium phosphate containing about 0.001 per cent of titanium salt gave a considerable increase in the corrosion-resistance of the phosphate film, even when the latter was unprotected by an organic coating. In preparing the titanium dip it is apparently necessary to add the titanium salt to the original disodium phosphate solution at the time it is made up and to evaporate to dryness in the presence of the titanium ion; the simple addition of a soluble titanium salt to a 1 per cent solution of disodium phosphate results in a bath which is relatively inactive.

Flexible Phosphate Coatings. Another advance in phosphate coating has been the development of a process to enable steel or other sheet metal to be treated so that a film is produced which will be sufficiently tenacious to enable forming and drawing operations to be carried out after painting or lacquering (B.P. 557,846 (1943)). This method is especially useful in the manufacture of food cans, milk-bottle caps, instrument panels, etc., where it is highly advantageous to produce the articles from sheet metal which will require no further finishing treatment.

The essential feature of the method is the application of a very thin phosphate film (not exceeding 110 to 150 mgm. per sq. ft.) from a suitable solution. The film must be highly adherent and flexible. One solution recommended is prepared by dissolving in 180 gallons of water $7\frac{1}{2}$ lb. of a concentrate made by dissolving zinc oxide in phosphoric acid and adding water. The proportions are 49 per cent of 75 per cent phosphoric acid, 12 per cent zinc oxide, and 39 per cent water. To this are added $3\frac{3}{4}$ lb. of sodium meta-nitro-benzene sulphonate and 0.8 lb. of sodium hydroxide; these materials act as accelerators. The time of treatment is one minute, the temperature of the solution being 120° F. to 125° F. The film is preferably produced by passing the sheets between resilient rollers whilst they are being coated, as this accelerates the reaction and results in the formation of uniform films.

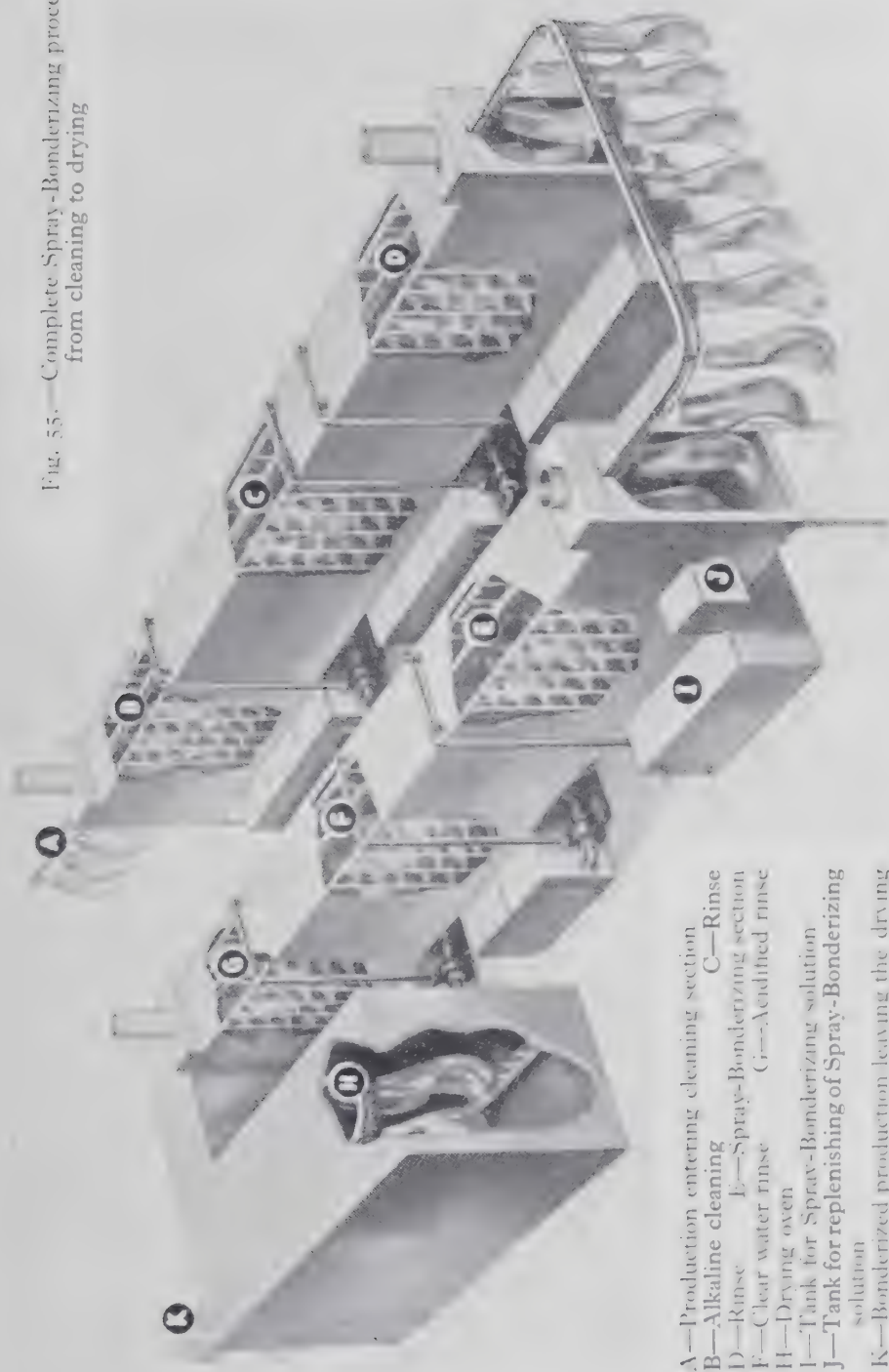
Naturally, lacquers and varnishes for application to the phosphate coat must themselves be carefully selected to possess adequate flexibility to enable them to withstand the necessary forming operations.

Phosphating Plant.—Plant for carrying out phosphate coating has in recent years been developed to a tremendous extent. Very large conveyerised installations have been built both for immersion and spray treatment on steel pressings for motor bodies, wings, headlamps, etc., since the advantages of such pre-treatment prior to painting are now widely recognised. The parts are jigged on special racks or frames and travel through the plant continuously.

In smaller plants, the treatment is carried out in steel tanks into which the articles are lowered on racks, wires, or in baskets. Rotating perforated baskets are also employed to provide more intimate contact of the solution with very small components; the perforations tend, however, to clog up with precipitated salts in time, reducing their efficiency. An ingenious type of automatic plant for dealing with small articles is the tipping basket machine in which the articles are transferred by tipping successively through a series of baskets, and thus through the whole treatment cycle.

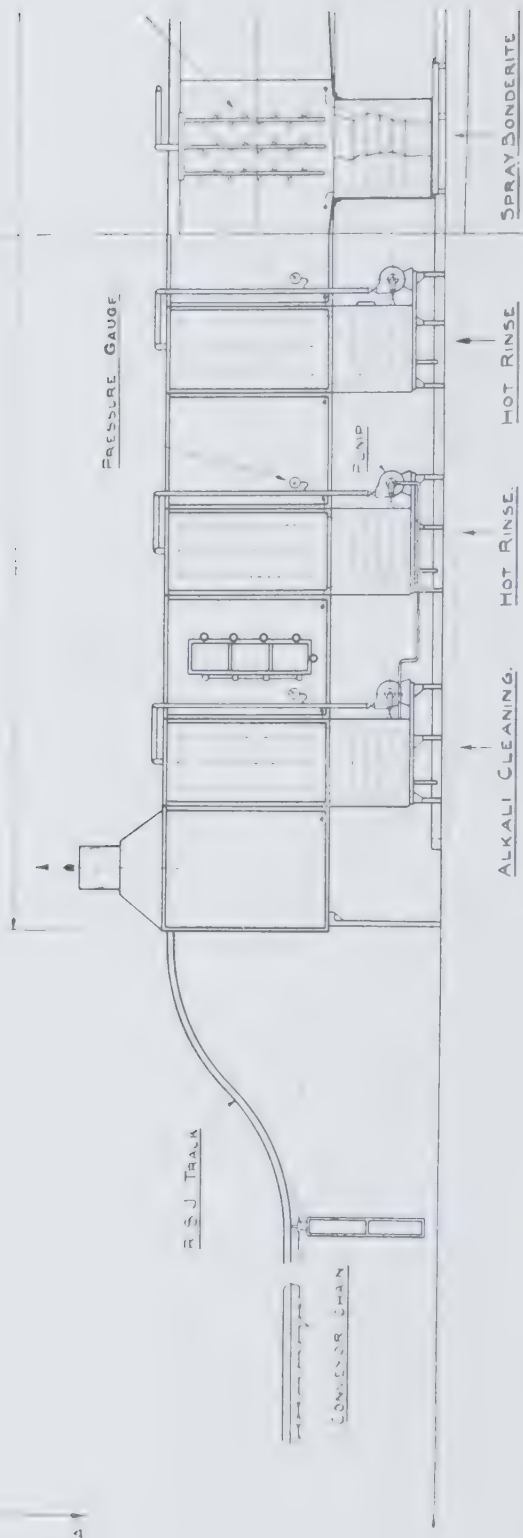
After prolonged use steel tanks become coated on the inside with a layer of insoluble phosphates, but such tanks will last for several years before failure eventually occurs, due to perforation of the steel by the solution. Stainless steel is not attacked by phosphating solutions, but plant constructed from this material is not in extended use on account of cost considerations. The best type of stainless steel for resistance to phosphate solution is the molybdenum-containing austenitic nickel-chromium steel, as this is less subject to pitting corrosion than the normal 18:8 nickel-chromium stainless steels. In addition,

Fig. 55. Complete Spray-Bonderizing process from cleaning to drying



- A—Production entering cleaning section
- B—Alkaline cleaning
- C—Rinse
- D—Rinse
- E—Spray-Bonderizing section
- F—Clear water rinse
- G—Acidified rinse
- H—Drying oven
- I—Tank for Spray-Bonderizing solution
- J—Tank for replenishing of Spray-Bonderizing solution
- K—Bonderized production leaving the drying oven, ready for final finish

B

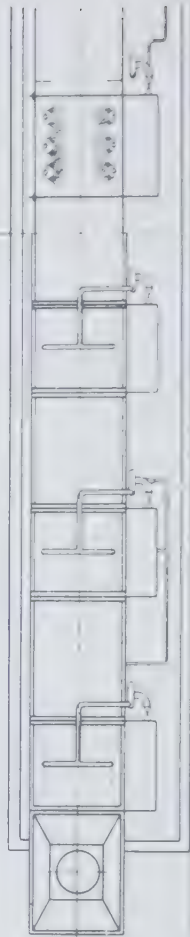


B

PART SECTIONAL

TENSION SPROCKET

DIRECTION OF WORK



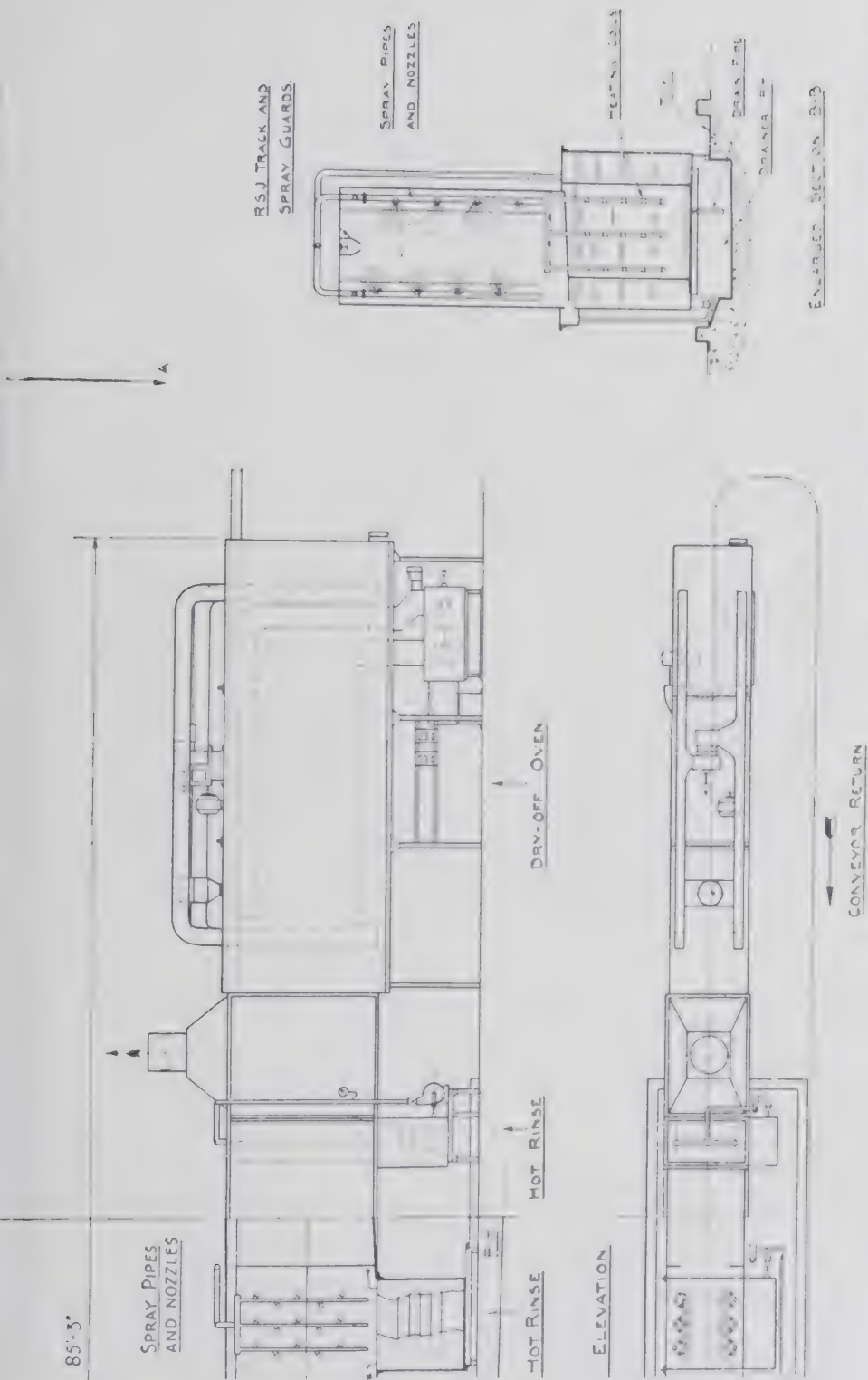


Fig. 56.—General arrangement of phosphating plant for the treatment of motor-car lamp bodies prior to painting

(Courtesy of F. J. Ballard & Co. Ltd., and Joseph Lucas Ltd.)

welds may not withstand the action of the solution as well as does the general stainless steel surface. Nevertheless, several large plants have already been constructed, and it is possible that the use of stainless steel in phosphatising plant will extend.

Perhaps the most satisfactory material of construction, especially for spray-plants, is hard rubber-lined steel. The rubber when correctly bonded to the steel will last almost indefinitely. It has, however, the disadvantage of mechanical weakness and may be damaged if jigs fall on to it, or when the plant has to be entered for



Fig. 57.—Immersion Bonderizing plant for treatment of wheels

cleaning purposes. To reduce this danger rubber mats may be laid on the tank floor, or alternatively the bottom may be lined with acid-resisting tiles.

The heating of phosphating plant presents considerable difficulties. Usually, copper steam coils are employed, but the sludge precipitated in the solutions during working forms hard, coherent deposits which can only be removed with great difficulty, usually by chipping them off. The sludge as formed is light, but as it accumulates on the hot surfaces it becomes extremely hard and reduces the heat transfer efficiency of the coils rapidly. It has already been pointed out that a relatively small reduction in temperature results in a considerable lengthening of the time required for the formation of a satisfactory phosphate coating; for this reason any lowering of the bath

temperature is very undesirable. There is some advantage in circulating the solution by means of a pump through a relatively coarse filter to remove sludge, and this procedure has been adopted with some success in recent installations. Such filters tend to become clogged rather quickly, however, and alternative methods have been experimented with to facilitate separation of sludges. Settling tanks are useful, but they are bulky and require frequent cleaning. Centrifugal separation is the newest method to be tried, and results obtained indicate that this procedure is likely to prove particularly useful.



Fig. 58. —Typical arrangement of manually operated Parkerizing plant

Gas-heated tanks are also employed, but here again the accumulation of scale on the tank results in poor heat transfer in time. Moreover, gas-heating cannot be applied easily to rubber-lined plant.

Fig. 55 shows diagrammatically the sequence of operations in spray-Bonderizing plant. Fig. 56 shows the lay-out and construction of a typical plant, whilst Figs. 57 to 60 are views of different types of phosphatising installations.

Roto-dip Plant.—Perhaps the greatest achievement in the field of automatic phosphating plant has been the design and construction of the Roto-dip unit. Produced primarily for the finishing of automobile bodies, Roto-dip cleans, pre-treats and dip-paints complete

motor-car bodies entirely automatically. The bodies are fixed to special suspender bars passing longitudinally through them, and they are then transferred laterally through an alkaline cleaner solution, rinses, Bonderizing tank, further rinses, and drier. They finally enter the paint primer tank where they receive a coat of a suitable alkyd paint, and after draining this is stoved in an oven at about 250°F .

During the whole of these operations the bodies are rotated continuously at carefully controlled speed to ensure that the processes



Fig. 59.—Spray-Bonderizing plant for motor-car wings

are carried out uniformly and completely. Control of paint viscosity is of great importance to ensure that the paint flows uniformly over the surfaces to be treated and to ensure that these are free from sags and runs. In view of the large quantities of paint used, careful precautions must be taken against fire, and these include provision for dumping the paint into an underground tank should fire break out, and the installation of carbon dioxide extinguishing equipment.

A complementary process is the Roto-spray arrangement in which the bodies are not dip painted, but rotated in spray booths in which the paint can be applied by hand from spray guns. This makes for the ready accessibility of all parts to be painted to the spray gun. Roto-spray enables the finishing coats to be applied to the bodies after the primer has been stoved on in the Roto-dip unit.

“OXIDISED” FINISHES

The well-known “oxidised” copper and silver finishes which are applied to steel and also to non-ferrous metals are decorative, and very suitable for indoor conditions where they are capable of giving good service.

“Oxidised” copper is produced on steel by first plating in a cyanide solution to give a thin copper deposit, which does not usually exceed 0.0001 in. in thickness. (See p. 334.) The article is then brushed with

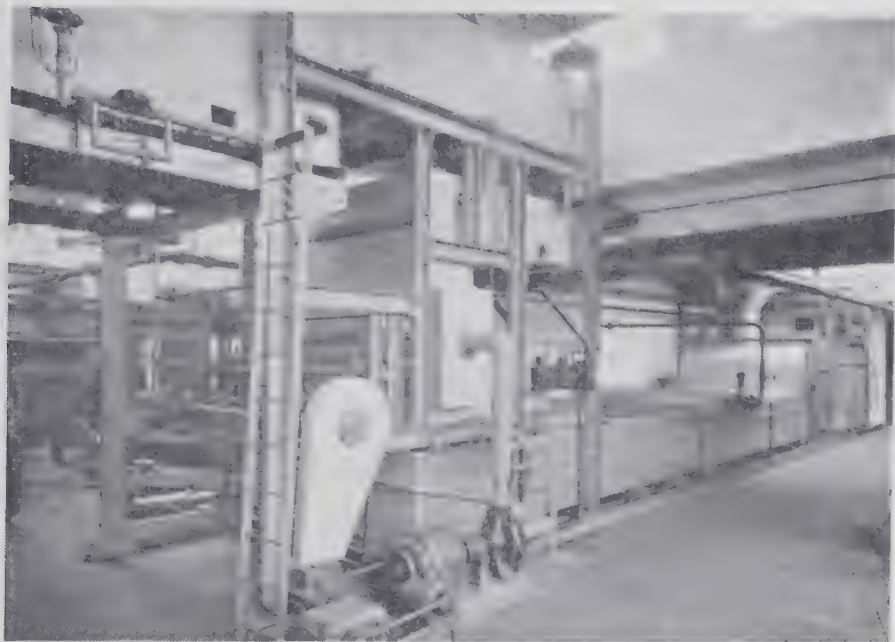


Fig. 60.—View of Bonderizing plant showing pumping unit

or immersed in a dilute solution of ammonium sulphide; or potassium or sodium sulphide solutions may be employed. Sometimes ammonium chloride is added. The duration of immersion and the concentration of the solution determine the depth of colour produced, but in order to obtain attractive and uniform colouring, much depends on the skill of the operator.

It is desirable to use dilute sulphide solutions, since these enable greater control to be exercised over the darkening process, whilst the sulphide films are more closely adherent than when more concentrated solutions are employed.

After rinsing and drying in sawdust, the parts are often improved in appearance by a “relieving” operation, which consists in removing

the sulphide deposit from the high-lights by hand-rubbing or wet scratch brushing, using pumice powder.

The "oxidised" silver finish is likewise applied by plating with a thin coat of silver and then immersing in a sulphide solution in the same way. Barium sulphide solutions have also been successfully employed with silver deposits. Silver can be "oxidised" in a dilute solution of platinum chloride. In this way attractive tones can be produced as a result of the deposition of finely divided platinum on the silver surface: $4\text{Ag} + \text{PtCl}_4 = \text{Pt} + 4\text{AgCl}$. This process is necessarily more costly than those previously described, and for this reason is relatively little used.

The ease with which a whole range of browns and greys, and also black, can be produced by sulphide treatment, makes this method of finishing a very popular one. The sulphides, however, unfortunately lack stability, and are prone to undergo re-crystallisation changes, so that local discoloration of the coating, sometimes termed "sulphur spotting", is liable to take place.

Miscellaneous Methods of Colouring Steel.—Other processes for the colouring of iron and steel are much less commonly employed than those described above. Like the "oxidised" finishes, they do not usually produce good results by simple immersion. Scouring, rubbing, or brushing whilst the metal is in contact with the solution, are essential to the development of a satisfactory colour.

The selenious acid method finds application when a dark grey or black colour is required.

The solution employed consists of:

Selenious acid	1½ oz.
Copper sulphate (cryst.)	3 oz.
Nitric acid (sp. gr. 1.2)	1½ fl. oz.
Water	1 gallon

Another method makes use of the interference colours produced by a film of lead oxide precipitated on to the steel surface by immersion in a solution consisting of:

Lead acetate	1½ oz.
Sodium thiosulphate	1½ oz.
Water	1 gallon

The solution is employed at a temperature of 120° F.

By controlling the time of immersion, a series of colours, ranging from yellow through red to purple and blue-black can be obtained.

Steel Bronze.—A steel bronze finish can be produced on ferrous metals by treatment in a solution of arsenic, which is deposited on the metal surface slowly. A solution of this type contains:

Arsenious oxide	.	.	.	20 oz.
Copper sulphate	.	.	.	10 oz.
Ammonium chloride	.	.	.	2 oz.
Hydrochloric acid	.	.	.	1 gallon

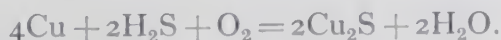
The arsenious oxide is dissolved in the hydrochloric acid, whereby a solution of arsenic trichloride is produced, after which the other constituents are added. The quickest results are obtained by using the warmed solution. The deposit can then be very lightly buffed and lacquered.

This solution will also produce a similar finish on tin, zinc, and on cadmium deposits, but should be diluted ten or fifteen times for use on these metals.

A number of attractive colours and effects can be obtained on copper, and these can be produced similarly on iron and steel if the metal is first copper-plated. Electro-plating in a cyanide solution is to be preferred, but coppering by immersion without current in a copper sulphate solution is sometimes practised. Where better protection is required, a greater thickness of metal is applied from an acid copper sulphate bath after the initial deposit of cyanide copper.

Copper and its Alloys. Copper and copper alloys are usually coloured various shades of brown, as this is the type of colour that is most readily obtained and is attractive in appearance. With copper alloys, the development of the colour depends almost entirely on the copper constituent, since the other metals usually present do not form coloured compounds during the treatment.

When copper is immersed in solutions of sulphides, combination takes place:



Air and moisture are essential for the reaction.

The alkali sulphide solutions (sodium and potassium sulphides) and ammonium polysulphides are all effective at room temperature. As the temperature increases, the reaction is accelerated; thus a 10°C . rise of temperature approximately doubles its speed. Increasing the concentration of the solution has a similar effect.

A typical solution would consist of about 2 oz. per gallon of potassium sulphide, the bath being maintained at a temperature of 160°F . The parts are immersed in the solution and brushed or

scoured until the desired shade of colour is obtained, after which they are rinsed, dried off in sawdust and "relieved" by rubbing with pumice powder if necessary. The exact shade of colour produced can only be gauged by experience in each case, since the colour is not only influenced by the temperature and time of treatment, but also by the composition and physical structure of the alloy. Thus castings generally give a different type of colour than fabricated metal, and it is not usually practicable to match the two shades. In such cases it may be desirable to copper-plate the parts concerned if a true match is desired.

The treatment is usually carried out in the form of several "cycles" until the required depth of shade is obtained, viz. cleaning in an alkaline solution followed by rinsing, immersing in the sulphide, rinsing again, and then immersing for a few seconds in a 2 per cent sulphuric acid solution to neutralise residual alkali. The articles are finally washed once more and dried off in sawdust, after which they are scratch-brushed or "relieved", using wire or tampico brushes, wet pumice or sometimes buffing compounds on calico buffs. As the durability of these finishes is poor unless they are protected, a good quality hard transparent lacquer is applied after treatment, usually by spraying.

Small components may have the "high-lights" relieved by treatment in a barrel with pumice and sawdust after lacquering, and are then finally relacquered.

Thioantimoniate Solutions.—Solutions of sodium thioantimoniate react with copper and brass with the deposition of sulphide deposits having an attractive glossy appearance. The thioantimoniate can be applied either by dipping or brushing. Acidification of the solution accelerates the reaction by liberating sulphuretted hydrogen, but this procedure removes one of its advantages, i.e. the fact that the solution develops little odour, as compared with the pronounced unpleasant fumes given off by the other sulphiding solutions already described.

It is often better to dip the article alternately into the thioantimoniate solution and then into a very weak solution of sulphuric acid if accelerated colouring is required. More rapid darkening can be obtained by using a dilute solution of mercuric nitrate in place of sulphuric acid. Thioantimoniate solutions are commonly used in strengths of 2 to 4 oz. per gallon and give particularly uniform colouring.

Other Methods.—Other methods of colouring copper and its alloys make use of various solutions containing certain salts of metals such as lead, tin, antimony, arsenic, etc. From these, deposits of

the sulphides of the latter metals are precipitated. The salts employed include tartrates and thiosulphates, and colours ranging from light brown to greys and black can be obtained.

A solution of this type is made by mixing equal parts of solutions containing 20 oz. per gallon of sodium thiosulphate and 16 oz. per gallon of lead acetate, respectively. By immersion in this solution at temperatures of 100° F. to 140° F. colours ranging from yellow to blue can be produced, depending on the temperature and the time of immersion. By increasing the thiosulphate content the rate of colouring is increased, as is also the case when a small excess of tartaric or acetic acid is present. The parts are well rinsed and dried after treatment.

Fused Salts.—Copper and its alloys can be coloured by treatment in molten salts. Thus, by immersion in sodium nitrate for five minutes at 350° C. to 450° C. copper acquires a red colour. The nitrite can also be used, as can mixtures of the two salts. The parts must be dry and free from grease, as ignition of such foreign material on the metal surface may take place on immersion in the fused mixtures, with the result that the salt will splash and may cause burns to the operator. The deposit consists of an oxide layer; it may be lacquered directly or, better, dipped in molten paraffin-wax, buffed, and then lacquered. The use of fused salt is, however, awkward, and demands fairly elaborate equipment and careful handling of the parts being treated. The method cannot, moreover, be used on parts which are too large for immersion in the bath, so that its use is generally limited to the treatment of small components.

The oxide finishes tend to be more durable than the sulphide coatings, owing to the instability of the latter compounds and their liability to internal re-crystallisation, as has already been pointed out.

Black for Copper Alloys.—Copper and its alloys can be coloured a deep black by immersion in a solution containing:

Caustic soda	1½ oz.
Ammonium persulphate	½ oz.
Water	1 gallon

The bath is used at boiling-point, a period of about five minutes being required for the development of the colour. A slow evolution of oxygen from the solution takes place during the process. The parts are rubbed after treatment, when a black matt finish develops.

The solution decomposes gradually, so that additional persulphate must be added from time to time in small amount. This treatment is applicable to a very large range of copper alloys.

Potassium permanganate can similarly be employed in alkaline solution as the oxidising agent, but the colours lack the dense black appearance of those obtained from the persulphate bath. They are, however, useful where brownish shades are not objectionable. Solutions of ammonium sulphate or nitrate produce slate-grey colours on copper and its alloys.

Green Patina.—The green patina which develops on old copper after prolonged ageing in the atmosphere consists almost entirely of the basic sulphate of the metal, and approaches the composition $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$.⁽²²⁾ When formed under natural conditions the coating is tenacious and durable and protects the underlying metal against further attack very well. This accounts for the fact that copper roofs hundreds of years old are still giving service in various parts of the world. The patina appears to show little increase in thickness after a prolonged period, reaching a stable condition.

The appearance of the patina can be approximately imitated by various treatments, although such coatings do not have the weather resistance of the deposit naturally developed under suitable conditions. One method recommended by Kushner⁽²³⁾ consists in applying to the metal a paste made from:

Basic copper acetate . . .	3 lb.
Copper carbonate . . .	1 lb.
Ammonium chloride . . .	3 lb.
Hydrochloric acid . . .	1 quart
Arsenious acid . . .	$\frac{1}{2}$ lb.
Water . . .	Sufficient to make a paste

The paste is allowed to remain in contact with the metal surface, being worked in well by means of a brush and allowed to dry for two or three days. After this the residue is brushed off, and the process repeated until the desired shade of colour is obtained. The coating produced in this way is said to be very adherent.

An alternative procedure is to use the following solution:

Copper nitrate . . .	2 lb.
Ammonia . . .	3 lb.
Ammonium chloride . . .	4 lb.
Sodium acetate . . .	4 lb.
Water . . .	1 gallon

This is used as a dip, being allowed to dry on to the metal, the treatment being repeated as desired.

A method for producing an artificial coating approaching the natural patina in composition consists in treating the article twice daily for a week with a 10 per cent solution of ammonium sulphate, and then for a further two days with a 10 per cent solution of copper sulphate containing about 1 per cent of sodium hydroxide. No further protection is then required. The method is said to be particularly successful with arsenical copper.

Vernon⁽²⁴⁾ also describes a superior method for producing the patina. This consists in anodically treating the metal in a solution of:

Magnesium sulphate	.	.	10 per cent
Magnesium hydroxide	.	.	2 per cent
Potassium bromate	.	.	2 per cent

The solution is kept at about 95° C., treatment being continued at a current density of about 0.4 amp. per sq. ft. for fifteen minutes. Initially, the deposit has the composition $\text{CuSO}_4 \cdot \text{Cu}(\text{OH})_2$, but gradually increases in basicity on exposure until the composition of the patina is reached.

Brass.—Colours can be produced on brass by processes similar to those employed in the case of copper. Owing to the fact that, with a few exceptions, zinc compounds are not coloured, practically the entire effect is due to the copper constituent of the alloy. Special difficulties may arise with certain types of brasses. Thus, the free-machining lead-bearing brasses may cause trouble during sulphide treatment because of the development of black spots at local inclusions of lead. Likewise the pre-cleaning treatment before colouring may bring about changes and non-uniformity in the initial colour of the brass which will result in variations in the final appearance of the finish. Cathodic alkaline cleaning may result in dezincification of the metal and re-precipitation of metallic zinc on the surface, with a lightening of the colour of the brass and hence of the coloured film. Acid-dipping, if it is to be carried out, may, on the other hand, redden the colour of the brass. This is not caused directly by preferential dissolution of the zinc, but is a secondary effect resulting from the re-precipitation of copper which has dissolved in the cleaning acid by chemical interchange with the zinc in the brass. Preliminary cleaning processes therefore demand careful attention.

Besides the treatments already described for copper, brass can be given a pleasing golden brown coloration by immersion in a solution of neutral copper acetate maintained at a temperature of 160° F. for a short time.

Brass can be coloured black by immersion in an ammoniacal

solution of copper carbonate; the black usually has a bluish cast. A typical solution has the composition:

Copper carbonate	2 lb.
Ammonia solution (sp. gr. 0.88)	1 gallon
Water	1 gallon

Hogaboom⁽²⁵⁾ describes a method for producing a range of sulphide colours on bronzes or high copper alloys generally. A sand-blasted surface is "oxidised" in a sulphide solution and scoured with sand, leaving a dark shade in the recesses. After drying, a clear lacquer, high in gum, is applied and dried in an oven at a temperature that turns the lacquer a light brown. While still warm, the article is brushed with a goat's-hair wheel to which is applied a wax in which has been incorporated a pigment. If turmeric is mixed with equal parts of bees and carnauba wax and applied in this way, an attractive shaded golden bronze can be produced.

Cadmium.—Cadmium can be blackened by immersion in a hot lead acetate-sodium thiosulphate solution similar to that used in the treatment of copper alloys (see p. 186) e.g.:

Lead acetate	$\frac{1}{4}$ oz.
Sodium thiosulphate	12 oz.
Water	1 gallon

The deposits are, however, inclined to be powdery and to have poor adhesion. The copper sulphate-potassium chlorate-sodium chloride bath gives a denser black finish, which is more adherent.⁽²⁶⁾ The solution used consists of:

Copper sulphate	$2\frac{1}{2}$ oz.
Potassium chlorate	3 oz.
Sodium chloride	3 oz.
Water	1 gallon

The temperature is of the order of 180 F. to 200 F. and the solution is employed in a rubber-lined or stoneware container. If there is any tendency for basic salts to be precipitated, resulting in a "bloom" on the work, a few drops of sulphuric acid should be added. The time of immersion need only be a few seconds.

In this solution a three-stage reaction takes place. Copper is first precipitated by interaction with the metallic cadmium, and this is oxidised by the chlorate first to the reddish cuprous oxide, and then to black cupric oxide. Rapid movement of the articles while in the solution results in the deposition of the copper in a compact form so that the resulting black film is more adherent.

After treatment is complete, the parts may be lightly brushed with steel wool or pumice and lacquered. This produces a useful imitation pewter finish.

A brown colour can be produced on cadmium by treatment in a solution of:

Potassium dichromate	.	.	1 oz.
Nitric acid (sp. gr. 1.2)	.	.	$\frac{1}{2}$ oz.
Water	.	.	1 gallon

The articles are immersed in the solution which is maintained at a temperature of 140 F. to 160 F. A pale yellow colour is developed at first, but on continued immersion for two to four minutes, a rich mahogany colour is formed. Further immersion produces still darker colours. The appearance can be improved by polishing the "highlights" on a buff using a tripoli composition.

The film has good adhesion and durability; additions of dichromate and nitric acid have to be made to the bath from time to time, but excessive amounts of nitric acid are to be avoided or the film will be poor. The finish applied on cadmium plate is used for imitating old silver; it is, however, inadvisable to use cadmium plate on utensils required for foodstuffs owing to the toxicity of the metal.

An antique brown shade on cadmium is also produced by immersion in a hot solution containing:

Copper sulphate	.	.	$\frac{1}{4}$ oz.
Ferric chloride	.	.	2 oz.
Hydrochloric acid	.	.	10 fluid oz.
Water	.	.	1 gallon

The solution is used as hot as possible, the articles being immersed and allowed to dry without rinsing. The treatment is repeated until the desired shade of colour is obtained.

The more recently developed permanganate solutions for producing durable colours, ranging from yellow to deep brown, are worthy of mention. These solutions in addition to the permanganate, contain cadmium nitrate, potassium chlorate, and sometimes ferric chloride, copper nitrate, etc. A deep brown is produced from a solution containing:

Potassium permanganate	.	.	40 oz.
Ferric chloride	.	.	3 oz.
Cadmium nitrate	.	.	15 oz.
Water	.	.	1 gallon

Darker shades are produced by an increased proportion of permanganate.

The bath is used hot (about 180°F.). If the solution becomes turbid, a few drops of nitric acid should be added. For the best results it is desirable that the colouring operation be carried out directly after plating and before there has been an opportunity for an oxide film to form on the plated surface.

The molybdenum colours are useful on cadmium and also on zinc plate. Thus immersion in a solution of:

Ammonium molybdate	.	.	2 oz.
Ammonium chloride	.	.	4 oz.
Potassium nitrate	.	.	1 oz.
Boric acid	.	.	1 oz.
Water	.	.	1 gallon

for a few seconds results in a fine adherent black deposit of molybdenum sesquioxide. The solution is used hot at a temperature of 140°F. to 160°F.

Coloured cadmium-plated finishes are very useful, especially on steel, because of the high corrosion resistance of the initial cadmium deposit. Their resistance is, in particular, considerably better than the bronze finishes applied by colouring steel after copper or brass plating. Even without lacquering coloured cadmium deposits produced by the dichromate-nitric acid method will withstand quite appreciable exposure to weather. This is certainly not the case with the finishes of the copper- and brass-plated types.

Zinc.—The colouring of zinc, like cadmium, presents difficulty owing to the fact that the salts of the metal are practically all colourless. A common method of producing a black finish makes use of immersion deposits of nickel obtained by dipping the articles in a solution of nickel sulphate or nickel ammonium sulphate. Additions of sodium thiocyanate, iron or ammonium salts are sometimes made. The colours thus obtained are black or grey, depending on the exact composition of the solution and time of immersion.

Buffered solutions of molybdenum salts are likewise employed; these are kept slightly on the alkaline side, at a pH of 8.5 to 9.5. They may be used hot or cold, the time of immersion varying from one to five minutes. This time is important as excessively prolonged immersion causes flaky coatings to form, whilst poor or irregular coloration results from too short an immersion period. The coatings when correctly applied are quite tenacious and adherent. A slightly

acid solution of ammonium molybdate will colour zinc black; the addition of chlorides or fluorides accelerates the reaction.

Zinc deposits, like cadmium, can be coloured black in the copper sulphate-sodium chlorate solution, and the permanganate types of bath already described for cadmium.

Zinc-base die-castings are sometimes copper-plated in a cyanide solution and the latter metal is then coloured. This is not a really satisfactory procedure, however, owing to the fact that the copper tends to be absorbed gradually by the zinc, so that the colour disappears.

Perhaps one of the best methods of colouring zinc black is to apply a "black nickel" deposit. This consists in plating on to the zinc at low current density (about 2 amps. per sq. ft.) from a solution of a nickel salt containing zinc sulphate and thiocyanate. A representative formula for such a solution is:

Nickel sulphate	16 oz.
Zinc sulphate	4 oz.
Sodium thiocyanate	2 oz.
Water	1 gallon

The solution may be used cold, the anodes being of nickel, or stainless steel. The deposit consists largely of nickel sulphide, together with some occluded organic substances.

A method of depositing a green nickel subsulphide has been described.⁽²⁷⁾ The solution used consists of nickel ammonium sulphate, 100 gm.; sodium thiosulphate, 10 gm.; sodium citrate, 15 gm.; water, 1 litre; pH 6.4. The current density used ranges from 0.1 to 15 amps. per sq. ft., depending on the colour and structure of the deposit required.

"Cronak" Process.—This process enables an iridescent golden film to be applied to zinc or zinc-plated components, which has considerable value in preventing the formation of white corrosion products on the surface of the metal. It is not claimed, however, that it will materially increase the protective value of zinc as a rust prevention under outdoor conditions.⁽²⁸⁾

Essentially the method consists in immersing the zinc in the wet condition after cleaning in the usual way in a solution consisting of:

Sodium dichromate	200 g./l.
Sulphuric acid	6 to 9 c.c./l.

The time of immersion is about ten to twenty seconds; the temperature of the solution should be kept at about 70°F. for the best results.

After treatment, the articles are rinsed thoroughly and dried, preferably by means of a warm air blast at not too high a temperature (below about 50° C.). Hot-water drying is not recommended, as this may result in the formation of films of low protective value.

The film consists of basic chromium chromate, $\text{Cr}_2\text{O}_3 \cdot \text{CrO}_3 \cdot \text{XH}_2\text{O}$, or $\text{Cr}(\text{OH})_3 \cdot \text{Cr}(\text{OH}) \cdot \text{CrO}_4$. A typical film weighs about 0.1 gm. per sq. ft. and is 0.00004 in. thick. The protective value is said to depend on the slow release of the hexavalent chromium from the film to the water which comes into contact with it, and this has an inhibiting effect on the development of corrosion.

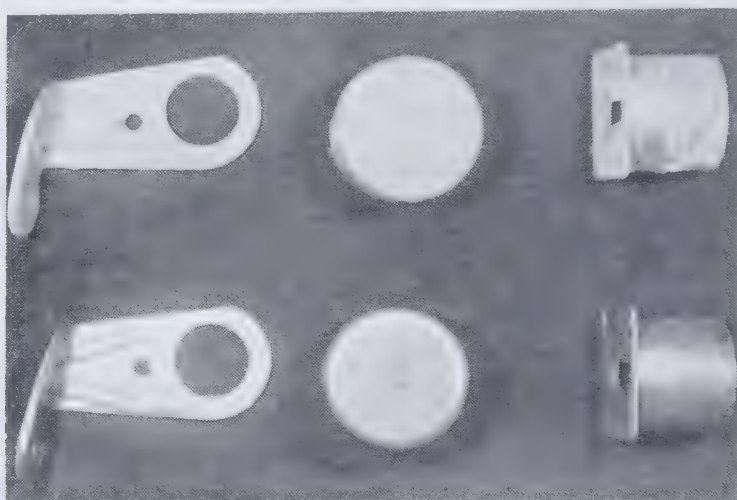


Fig. 61.—Zinc-plated components after 200 hours' salt-spray. Those in the lower row were Cronak-treated; those in the upper row were not treated

Fig. 61 shows the appearance of zinc-plated components with and without "Cronak" treatment after exposure to salt-spray for 200 hours. Table XXXI gives some test results under experimental conditions of exposure. Chromate passivation is discussed in greater detail later in this volume (p. 400.)

Lead.—Lead when exposed to weather acquires a grey patina which is normally very thin, dense, and highly durable. Artificial patinas, on the other hand, are much softer and less durable, although they may be useful in some cases, especially if lacquered.

Lead must be cleaned before any chemical treatment is applied by washing with an alkaline solution of a mild type such as trisodium phosphate with or without the addition of sodium carbonate.

Black or dark colours are produced by dipping in a solution of yellow ammonium sulphide or in a solution containing 10 per cent

TABLE XXXI

CRONAK PROCESS

RESULTS OBTAINED ON ZINC BOTH TREATED AND UNTREATED
UNDER VARIOUS CONDITIONS OF EXPOSURE

Type of test	Time to first white salts—days	
	No treatment	"Cronak" treated
95° C. Steam	1	12
40° C. Steam	1	182
Salt-spray	8 hours	91-104 hours
Distilled Water	1	38

of ferric chloride in a 50 per cent solution of hydrochloric acid. A jet-black finish can be obtained by treating the metal with hydrochloric acid and then heating gently with a blow-lamp.

An antique green patina can be formed by dipping the lead into a warm solution containing:

Copper nitrate	10 oz./gallon
Ammonium chloride	5 oz./gallon
Acetic acid	5 oz./gallon
Chromic acid	1 oz./gallon

Alternatively the solution may be brushed on to the lead surface, after which the article is rinsed, dried and lacquered.

Nickel.—Nickel is a difficult metal to colour satisfactorily. The persulphate method is one of the best for obtaining a black film, a suggested solution consisting of

Ammonium persulphate	2 lb.
Sodium sulphate	1 lb.
Ferric sulphate	1½ oz.
Ammonium thiocyanate	1 oz.
Water	1 gallon

The solution is adjusted to a pH of 1 to 2 and is used at room temperature.

Aluminium.—This metal is best coloured by the anodic oxidation process (see p. 414), followed by dyeing or impregnating the film with a suitable dye. The metal is made the anode in an electrolyte such as sulphuric acid, or chromic acid, whereby a tenacious oxide film is

produced which can be directly dyed by means of appropriate dye-stuffs to almost any colour. The dyed films can then be "sealed" by after-treatment, e.g. in hot water at a pH of 6, in a solution of sodium silicate, or in a hot solution of a heavy metal acetate (e.g. cobalt acetate). The colours will then not leach out. Unlike most other metal-colouring processes, the films so produced are hard and durable and require no further lacquering or other protective treatment.

There are also non-anodic methods of colouring aluminium. An antique silver finish can be produced by treatment in a boiling alkaline arsenate solution containing 10 oz. of arsenious oxide and an equal amount of sodium carbonate per gallon of water.

Aluminium may be coloured blue by immersion in a solution containing:

Ferric chloride	.	.	.	75 oz.
Potassium ferricyanide	.	.	.	75 oz.
Water	.	.	.	1 gallon

This is used at a temperature of 160°F. The colour results from the precipitation of ferric ferricyanide in the pores of the thin oxide layer normally present on aluminium.

A black colour, which is not very dense, however, can be produced by immersion in an alcoholic solution of a cobalt salt, burning off the alcohol. The cobaltammines are useful compounds for this purpose; these are formed by adding ammonia to a solution of a cobalt salt until the precipitate which first forms just dissolves.

The molybdenum solutions and also the permanganate and copper sulphate solutions, which have been referred to for the production of black finishes on zinc and cadmium (p. 213) can be successfully employed with aluminium.

Gilding.—The deposition of gold on to metals, either electrolytically or by immersion, is practised as a common method of obtaining a pleasing colour. Coloured gold deposits can be produced by deposition from solutions to which various substances have been added. Thus, small amounts of silver salts will enable "green gold" to be deposited, the depth of green depending on the amount of silver present. Rose-gold is produced by the addition of alkalis such as sodium hydroxide or sodium carbonate to the plating solution, whilst copper salts darken the coloration obtained. This is the basis of "Russian" gold finishes. Attractive effects can also be produced in these processes by rubbing or "relieving" the high-lights of the articles.

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CHAPTER VI

ELECTRO-PLATING: MODERN PLANT AND EQUIPMENT

Electro-plating is one of the most important finishing processes because of the many advantages which plated coatings offer. Amongst the outstanding merits of electro-deposits are their hardness, uniformity, and the durability of even thin coatings.

The first metal to be electro-deposited on a commercial scale was probably silver. The purpose of such plating was then mainly decorative -viz. to reproduce the appearance of solid silver on articles made of cheaper metals, such as copper or brass. Modern electro-deposition is carried out not only for decorative purposes, but also to provide protection against corrosion and wear.

Principles.—In principle, electro-deposition is a simple process, and consists in making the article on to which it is desired to plate the cathode, or negative pole of a source of direct current in a suitable electrolyte. The positive pole, or anode, which is immersed in the solution is made of the metal being deposited, or of an inert material. The electrolyte consists of a solution of a suitable salt of the metal being plated, with or without various added substances included for the specific advantages to be gained by their presence. If the anode be of the same metal as that being deposited, it dissolves in the electrolyte, thus replenishing the metal content of the solution.

The industrial application of the principles of electro-deposition demands a considerable amount of care and attention if satisfactory results are to be obtained. Quantitatively, the process is based on Faraday's Laws of Electrolysis, which state that the amount of a substance liberated from a solution by electro-chemical action is proportional to the quantity of electricity passed, and that the amounts of different substances liberated by the same amount of electricity are proportional to their chemical equivalents. The chemical equivalent of every element is directly related to its atomic weight. The ratio of the atomic weight to the chemical equivalent is a small whole number termed the *valency*. The same element may have more than one valency. The *electro-chemical equivalent* of a metal is the amount of metal liberated by one coulomb of electricity (i.e. one ampere passing for one second).

Current Efficiency.—In actual practice the weight of a metal

deposited by a given quantity of electricity often differs from that calculated from Faraday's laws. Often the amount of metal obtained is rather less than that calculated, owing to a proportion of the current being consumed in the liberation of hydrogen and oxygen, or otherwise decomposing the solution. The percentages of the total current which result in dissolution of metal at the anode or deposition at the cathode, are termed the anode and cathode efficiencies respectively. Anode efficiency may exceed 100 per cent owing to chemical action which increases the amount of metal going into the solution beyond that due to electro-chemical dissolution.

It is desirable that both the anode and cathode efficiencies be as nearly as possible 100 per cent, as this causes the solution to maintain its composition without major alteration and results in the minimum wastage of current. Under carefully controlled conditions, it is possible to realise 100 per cent efficiency of deposition, especially with copper and silver solutions. This is the basis of the principle of the copper or silver *coulometer* which provides one of the most accurate methods of measuring quantities of current. In Appendix Table XIV are shown the electro-chemical constants of a number of metals commonly electro-deposited.

Solution Composition. The solutions employed in commercial plating processes have been evolved largely empirically, and can be broadly grouped into two types: (a) acid solutions, (b) alkaline solutions. The first group comprises solutions of what are often simple salts, usually with various additions, e.g. nickel sulphate or zinc sulphate solutions. In the second group the metal content is generally in the form of a less readily ionised complex salt, as in solutions of the cyanide group.

The commonest "acid" baths are simple salt solutions which may be operated either as neutral or acid baths (down to a pH of 2 or even less). They are characterised by their ability to work at fairly high current densities, and by the fact that they lend themselves to the building up of heavy deposits. As opposed to these advantages, they have two main disadvantages: (a) their relatively poor "throwing power", i.e. the solutions will not enable an adequate thickness of deposit to be obtained in recessed portions of articles of complex design without special anode arrangements, and (b) the fact that such solutions will generally deposit metal by chemical displacement when another metal lower in the electro-chemical series is immersed in them. An example of this is the deposition of copper on to steel when the latter is immersed in a solution of a simple copper salt;

such deposition will prevent satisfactory electro-plating. Complex salt acid baths are also used for some types of deposition, e.g. the fluoborate solution for the deposition of lead.

The alkaline solutions are typified by the cyanide baths consisting of the cyanide of the metal to be deposited, which is dissolved in a solution of an alkali metal cyanide, with a slight excess of the latter. In addition, a certain amount of carbonate will be present due to the action of the carbon dioxide of the atmosphere on the cyanide while other materials such as ammonia, caustic alkalis, tartrates, etc., may be added. The cyanide solutions have usually relatively good "throwing power" and can be used for deposition on to baser metals. Thus, a cyanide copper solution can be employed for plating directly on to steel or zinc. There is no deposition of copper until the current is applied. Other alkaline solutions, e.g. the sodium stannate solutions, are employed and some of these will be referred to when the deposition of specific metals is discussed.

Addition Agents.—Various substances are added to the plating baths in order to obtain particular advantages. In the case of nickel solutions, chlorides are generally added in small amount to promote anode corrosion. Nickel solutions also need to be operated within a limited pH range, and boric acid is used as a "buffering agent" to prevent too wide fluctuations in pH during operation. More recently, other additions have been made to plating solutions, with a view to obtaining bright deposits instead of the usual dull coatings. Organic materials (e.g. sulphonates) have been employed in nickel solutions as have also cobalt sulphate and sodium formate. Likewise, bright zinc deposits have been produced by the aid of molybdenum salts, or complex organic substances.

Throwing Power.—The problem of "throwing power" of a plating solution is a complex one which has been closely studied. In the deposition of a metal on to a complex-shaped surface there is a fundamental primary distribution of current. In the absence of "throwing power" this distribution would determine the ratio in which metal is deposited at any two given points on the surface. This primary distribution is often highly irregular and can be calculated; thus in a simple hemispherical cup 2 in. in diameter the ratio between the centre of the inside and the outside is 15.6 to 1.

By improving the throwing power of the solution this ratio can be improved. There are well-established methods of doing this, such as the use of complex metal salts such as cyanides for deposition which increase the cathode polarisation, and hence the throwing power of the solution.

Many of the factors conducive to high rates of deposition such as high temperatures and current densities, concentrated baths and agitation are unfortunately detrimental to the "throwing power" of the plating solution.

Plant Lay-out.—The lay-out of a plating plant needs the most careful consideration. The entire plant should be designed for flow production and reduce unnecessary movement of personnel or work to a minimum. Arrangement of the processes should facilitate the successive operations of polishing, pre-cleaning, racking, plating, unracking and inspection. Stripping of rejected work must also be catered for. Laboratory facilities in proximity to the plant are highly desirable. Another matter which tends to be overlooked often is the importance of providing adequate facilities for the maintenance and repair of plating racks, including rack insulation equipment.

Ventilation of the plating shop is an essential part of the installation, and provision must be properly made for intake of air into the shop to compensate for that removed by exhaust equipment.

Plating Plant.—Electro-plating plant requirements are rather critical as regards choice of materials because of the corrosive nature of the solutions used and the general conditions of service to which the plant is subjected.

An electro-plating installation would comprise the following main items:

- (1) Plating, cleaning, and washing tanks made of suitable materials.
- (2) A source of direct current supply at a low voltage (usually not exceeding 12 volts, although for anodising up to 60 volts may be required).
- (3) Heating plant for the various tanks.
- (4) Ancillary equipment, such as measuring and recording instruments, filtration units, pumps, air compressors or blowers for agitation of solutions, and exhaust ducts to remove noxious fumes.

TANKS

The material of which plating tanks are to be constructed depends a great deal on the nature of the solutions to be used. Cyanide solutions can be safely handled in iron or steel tanks, whilst acid solutions such as nickel and zinc sulphate were until recently almost always worked in lead-lined tanks. Chemical lead is generally specified, but antimonial lead has found favour on account of its greater hardness, especially for the lining of chromium-plating tanks.

A great many of the older lead-lined tanks were made of timber; such tanks are capable of giving many years of service and are still fairly extensively used. Lead-lined steel tanks are also employed, but these have the disadvantage that should perforation of the lead occur, the plating solution may then attack the steel. If a hole develops in the outer steel tank, repair is most difficult if not impossible. Perforation of the lead lining of a timber tank, on the other hand, shows itself in the form of a leak, and in such cases repairs are usually easily effected. The use of lead-lined steel is, therefore, confined largely to small tanks for dilute acid dipping, etc., rather than for large plating tanks.

It is often desirable that metallic or metal-lined tanks should carry an inner protective lining of some insulating material, to prevent short-circuiting as a result of articles or anodes touching the sides of the tank while attached to the support bars. Matchboarding has been widely used for this purpose in nickel-plating solutions, but the selected wood should be of a type which does not contain any appreciable amount of resin. Glass linings suspended from the walls of the tank and also laid on the bottom are better, and are used in chromium solutions where wood cannot be employed.

Rubber-lined Plant.—The technique of bonding rubber on to steel has revolutionised plating plant construction. It is now possible to vulcanise rubber directly to steel, the bond being so strong that the rubber will tear apart itself before it can be detached from the underlying steel. Rubber linings of this kind can be made in all grades of hardness from soft flexible linings to hard ebonite. For some purposes, composite linings of hard and soft layers are desirable. The hard rubber linings are rather more resistant to chemical attack and will stand higher temperatures than the softer rubbers; on the other hand, hard linings are more fragile and are likely to be cracked and damaged more easily than those of softer grades of rubber. Tanks of this type are very suitable for acid plating solutions at temperatures of up to 160° F., or even 180° F., but they should not be used with oxidising acids (e.g. chromic or nitric acids). Hard rubber linings will also successfully withstand most alkaline plating solutions operating at similar temperatures, and rubber-lined plants are in successful use with alkaline sodium stannate and copper cyanide solutions. Rubber lining has already been discussed (see p. 59) in connection with pickling tank construction.

The rubber compound used should be homogeneous and free from any constituents, such as heavy metal compounds, which might dissolve in the solution and contaminate it. This applies especially

to bright plating solutions. Insoluble fillers which have a tendency to work their way into the solution are likely to cause trouble by producing rough deposits, especially when any considerable thickness of metal has to be plated.

The advantages of rubber lining are considerable, inasmuch as a non-conducting surface is produced on the tanks, reducing the danger of short circuits and eliminating the need for inner matchboard or glass linings. Furthermore, increased flexibility of the plant is obtained, since the same tank can be used, if occasion demands, for such diverse solutions as nickel, tin, or copper, for instance. Should damage occur to the linings, repairs can be readily effected by local vulcanising. On the other hand, frequent inspection of the tank lining must be made as unrepaired breaks in the rubber can cause permanent damage to the steel tank which is most difficult to repair.

Adequate protection by suitable paints must be afforded to the outsides of tanks also, to prevent external corrosion by acids, etc., and they should be raised off the floor to minimise this risk. Rubber linings can be applied to wood and to concrete tanks; by suitable methods it is even possible to rubber-line old wooden tanks without removing them from their sites.

Vinyl Resin Linings.—For many applications the use of synthetic resin linings offers advantages over rubber and these are becoming increasingly employed. Vinyl co-polymers of the chloride-acetate type are the most successful of these materials and are resistant to oxidising acids and can be bonded to steel by special cements. Polyvinyl chloride can also be used. It is important that the resin should not contain excessive plasticisers and yet be sufficiently flexible to resist shock. In lining tanks with these materials the sheet of about $\frac{1}{8}$ in. thickness is bonded to the previously shot-blasted steel with the appropriate cements and joints are welded together usually with hot nitrogen. Jointing is the most difficult problem in the construction of plastic-lined tanks and must be executed with great care. Overlapping welds are the safest to use.

These linings tend to soften at temperatures above 150 F., and this limits their application. One advantage of such linings is that they are light in colour, which enables the interiors of plating tanks to be more readily seen.

Other materials for plating tanks have found some application. Vitreous enamelled iron vessels have been used, especially for precious metal-plating (since tanks for this purpose are generally quite small), while baths constructed from laminated thermo-setting resin materials on a fabric base (e.g. "Keebush") have also been

introduced to a small extent. Glass and glass-lined tanks, in which the glass linings are fused to the steel base, are still in the development stages, so far as plating practice is concerned.

Stray Currents. In the installation of plating plants, whether manually operated or automatic, attention must be given to ensuring that stray currents do not arise. Such currents can affect alkaline cleaners and result in stains developing on metal surfaces. Poor adhesion of subsequent deposits can also occur. Stray currents in alkaline copper, zinc and cadmium solutions have also been said to cause extreme roughness, lack of deposition of metal, poor adhesion and blistering.⁽¹⁾ The use of wetting agents in bright nickel solutions can be a source of trouble in the presence of stray currents, since the liberation of chlorine from heating coils which may become anodic, for example, can cause breakdown of the organic compounds used. Similarly lead can dissolve in the solution anodically and cause contamination of the solution.

Alternating or direct current can cause breakdown of organic brighteners, leading to the formation of a black scum on the bath. Bipolar effects can also occur where anodes hang too close to a heating coil or lose contact with the current-carrying bars.

To avoid the effects of stray currents tanks should be effectively insulated and heating preferably carried out in separate tank or heat interchangers. Ingoing and outgoing steam pipe-lines should have a section of high-pressure steam hose inserted in the line to avoid current leakage. Bus-bars should be thoroughly insulated at the supports.

A suggested method for detecting stray currents is to connect a pair of low-voltage light bulbs from the anode bar to earth and from the cathode bar to earth. The presence of stray currents will show itself by inequalities in the relative brightness of the two bulbs, whilst in extreme cases one bulb may fail to light altogether.

Stray currents in chromium-plating can result in the development of lack of throwing power or in effects similar to those arising from poor cleaning. High current densities may be needed whilst white or grey spots may develop having no apparent relationship to high- or low-current density areas.

Plating Barrels. Small parts are conveniently plated in inclined revolving barrels made of hardwood, ebonite, rubber-lined steel, or other suitable insulating materials. Phenol-formaldehyde resin impregnated laminated fabric has been used for barrels, but has the disadvantage of being somewhat attacked by alkalis. Melamine resins are rather more satisfactory in this respect. Cathode contacts

are built into the base of the barrel so that the parts are plated as it slowly revolves. An anode is suspended in the barrel, the anode-cathode distance being kept as small as possible. Contact is thus intermittent, but a reasonable thickness of plate can be built up if sufficient time be given.

Another type of barrel is mounted horizontally, being made of perforated insulating material, and operating in an outer tank of solution. The anodes are then suspended in the latter.

Fully immersed horizontal barrels give the most rapid rate of deposition as higher conductivity and longer contact times are obtained. A further improvement is to circulate the solution through the barrel by means of a pump, and so reduce ion depletion inside the perforated chamber. In the American "Mercil" barrel, which is of this type, it is claimed that forced circulation of the solution increases the rate of deposition of cadmium by 20 to 25 per cent.

Barrels of the first type are more readily manipulated, and can be tilted to enable the plated components to be discharged. Almost all metals may be plated in barrels, but it is often desirable to use special barrelling solutions of high electrical conductivity. Barrel-plating has the disadvantage that the tumbling action tends to remove a certain amount of metal during deposition, especially with the softer coatings, but on the other hand, it also results in a lustrous finish being produced. To minimise the tumbling action, loads in plating barrels should be kept small. An installation of a large number of small barrels is more satisfactory than a small number of larger ones for this reason.

CURRENT SUPPLY

There are only two methods for supplying current to plating plants in effective large-scale use. These are: (a) motor generators; and (b) metal rectifiers.

Motor Generators.—Motor generators for electro-plating purposes have been brought to a high pitch of efficiency and will give trouble-free service for long periods. There are certain special requirements for dynamos for plating purposes, and these requirements have to be met if useful service is to be obtained.

The four main types of windings used in generator construction are: (a) series winding; (b) shunt winding; (c) compound winding; (d) separately excited field coil winding.

Series-wound machines, in which the entire current developed passes around the field magnets, are simple to construct, but have the disadvantage that reversal of the polarity of the field magnets

may occur in some cases—e.g. if an appreciable polarisation current develops in the plating tank while the machine is running slowly. Furthermore, with increasing load there is a rapid increase in the voltage developed by the machine, which is undesirable. Series-wound machines are not suitable for plating purposes, and *shunt-winding* is, therefore, almost exclusively employed. Here a proportion only of the total current developed passes through the dynamo field coils, and can be controlled by a resistance. With shunt-winding, the current in the field coils is reduced as the load taken by the generator increases, so that in order to maintain a constant potential difference, the resistance in the field coil circuit must be gradually reduced.

Compound-wound machines are more satisfactory in that they are so designed as to make use of both series and shunt windings, and in this way it is possible to balance the opposing tendencies of the series windings to increase the current in the field coil windings as the current taken increases and of the shunt windings to reduce it. It is often desirable to have an “over-compounded” winding in which a slight increase of potential difference results when the load increases appreciably.

Separately excited machines enable the greatest control of current and voltage to be obtained. Where the main supply current to the motor is direct, separate excitation of the field coils is readily arranged, but in view of the fact that main current supplies are now usually of the alternating type, an additional dynamo driven from the main motor is required with this type of generator. The use of small rectifier units for field coil excitation is also becoming popular. Motor-generator sets usually operate from a main supply of 440 volts, and the current output may be as high as 5,000 amperes at voltages of from 6 to 12. The larger machines use multiple commutators to enable them to handle the large currents employed more easily. In Fig. 62 is shown a motor-generator set having an output of 1,500 amps. at 8 volts. Modern generators should have undercut mica separation between commutator bars to reduce brush wear and ensure satisfactory contact.

The armature core is built up of laminations insulated from each other to reduce eddy currents and radial ducts help to secure efficient ventilation. Bearings are of the ball or roller type and are separately housed in the case of large machines. Present-day opinion is that the length and diameter of the bearing should be about equal.

On larger generators the brush gear is carried by means of a rocker ring supported from the field magnet. The design of the ring permits the circumferential adjustment of the brush gear as a whole, means

for the radial adjustment of individual brushes being provided by axial serrations in the brush arms.

Field coils are of cotton-covered wire, the spool being fitted tightly over the pole to ensure good heat transmission and rigidity. The individual layers of the windings are first taped together, vacuum impregnated with varnish and stoved.

Rolled steel generator frames are to be preferred to cast iron, owing to their improved magnetic properties; steel will carry $2\frac{1}{2}$ times as

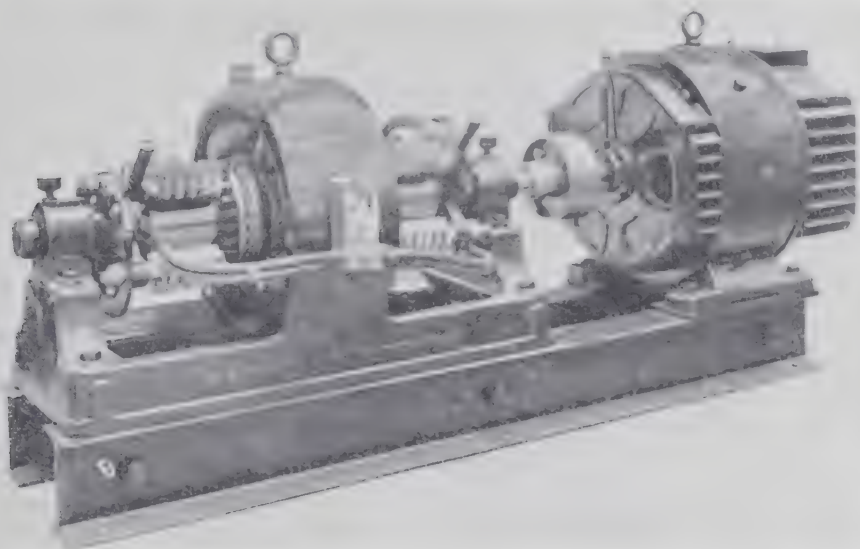


Fig. 62.—Motor-generator set having an output of 1,500 amps. at 8 volts

(Courtesy of W. Canning & Co. Ltd.)

much magnetic flux as cast iron. Armature supports are also better made of steel than of cast iron, whilst fabricated steel bed-plates are also becoming increasingly employed to reduce weight and obtain a stronger unit.

Brush maintenance is an important factor that must be reduced to a minimum in a good generator. Modern generators obtain good spark-free commutation by the use of accurately machined holders and the use of low brush pressures. In this way a brush life in excess of 15,000 hours can be readily obtained. To assist commutation, equalisers made of strap copper are fitted, and these also provide a degree of cooling for the generator.

METAL RECTIFIERS

The increasing use of metal rectifiers to supply current for plating purposes has been a feature of recent development in this field. Such

rectifiers have the advantage that, being static, there is less maintenance required, and the absence of vibration, coupled with the relatively light weights of the units, make them much favoured. The initial cost of a rectifier may be rather higher on large outputs than that of a motor-generator set having an equal output, but the advantages gained will more than offset any extra first cost.

Copper Oxide Rectifiers.—The copper-oxide rectifier was the first type to find large-scale application in electro-plating. Essentially, it consists of a series of copper plates assembled together; on each plate a thin layer of copper oxide is formed by heating to about 1000 C. The oxide film, as formed in this way, consists of an outer layer of cupric oxide, CuO , beneath which is another layer of cuprous oxide, Cu_2O , which acts as the rectifier; the cupric oxide surface must, therefore, first be removed, usually by chemical means. Rectification takes place owing to the far higher resistance offered to current passing from copper to cuprous oxide than to current passing in the opposite direction. Contact to the copper is made mechanically, and to the oxide film by volatising a layer of some suitable metal—e.g. zinc—on to the oxide surface and making contact to this.

A common plate size is 12 in. by 3 in.; both sides of the plate are oxide-coated and used for rectification. A small area of each plate is cleared of oxide to enable contact with the copper to be made, while contact with the oxide surface is obtained by the method already described. A suitable number of such plates are connected in parallel, several banks of plates being used together to give full wave rectification on single-, or more usually, three-phase current supply. The efficiency of a rectifier is often slightly superior to that of a good motor-generator set and is of the order of 70 to 85 per cent depending on conditions. Ashby⁽²⁾ describes a 1,000-amp. rectifier of this type operating at 8 volts; it occupies a floor space of only 4 sq. ft. and is 7 ft. in height. The step-down transformer stands alongside. Single units of up to 12,000 amps. output have been constructed.

In an emergency, rectifiers will stand considerable overloads for appreciable periods without incurring any damage, provided overheating does not take place; the temperature of a copper oxide rectifier must not be allowed to exceed 45°C.

Cooling.—The copper oxide rectifier plates are finned and are mounted in cabinets fitted with an overhead fan which draws air over the plate assemblies for cooling. Owing to the need for avoiding long lengths of bus-bar to carry the heavy currents, rectifiers are

often mounted in close proximity to plating or polishing shops, which may result in dust and dirt being drawn into the rectifier plates. A dust filter is therefore fitted*to prevent this occurring, but where contamination of the atmosphere is heavy, steps should be taken to install air-cooled rectifiers in a position where they will not be subjected to such conditions, even if additional bus-bar runs are required. The rectifying elements are usually coated with a bituminous paint to provide additional protection against corrosion.

Rectifier Current Control. A step-down transformer is, of course, an essential part of the equipment, and in the earlier sets control of the current output was obtained by using a single power transformer with various off-load tappings on the secondary winding. If the current had to be varied it was necessary to switch off and change the connections on the rectifier unit, owing to the technical difficulties of arranging for this to be done by "on-load" switchgear. On this account early rectifier installations were often operated in conjunction with resistance boards, as this was the only way in which adequate control of the plating current could be obtained.

As one of the outstanding advantages of a rectifier installation over a motor-generator set is that, correctly used, it provides a means of a wattless control of the power supply, the introduction of resistance was clearly undesirable. The next development was therefore the introduction of on-load tap-change gear operating on the primary winding of the transformer.

By means of an auto-transformer with two or three 4-position switches the voltage can be raised from zero to maximum in either eleven, fifteen, or sixty-three steps respectively; this range of control is more than adequate for practically all plating requirements. Where still finer current limits are necessary, a moving-coil or induction regulator which provides infinitely variable control can be employed. While such regulators are initially rather costly, they are extremely useful, particularly where operations requiring closely controlled current densities are being carried out (e.g. hard chromium-plating), and are being installed in increasing numbers.

Induction Regulators.—The induction regulator is similar in principle to an induction motor. The incoming supply is fed to the rotor of the unit so that a voltage is induced in the stator winding, the phase of which can be varied relative to that of the main supply. Thus by rotation of the rotor shaft the induced voltage in the stator can be caused to boost the main voltage and so enables the output from the regulator to be varied.

As the kVA of the regulator is determined only by the amount

which it is required to vary the throughput kVA about a mean value, its size need only be sufficient to provide the regulating kVA; this gives it an outstanding advantage over many other regulating devices.

The equipment can be air-cooled, but the majority of induction regulators are oil-immersed so that the size of the regulator frame can be kept to a minimum. Oil immersion follows the usual transformer technique, connection to the rotor being made by a suitable gear-box and drive. The regulator can be constructed for single- or three-phase operation over a suitable voltage range. The control is, nowadays, usually motorised on the larger installations so that regulation is carried out simply by means of a push button.

The Selenium Rectifier.—The selenium rectifier can be said to have practically rendered the copper oxide rectifier obsolescent for plating purposes because of the conditions under which such rectifiers are required to operate. Essentially the selenium element consists of an iron plate upon which a thin film of selenium is deposited, and this in turn is coated with a sprayed metal layer which acts as the counter-electrode to which connection is made. Again, the resistance to current travelling from the latter to the iron is far greater than to current travelling in the converse direction. Owing to the higher resistance of the selenium rectifier, less elements can be used in series for a given output voltage than with the copper oxide rectifier; the plates employed are similar in size and shape to those already described for the latter type.

The selenium rectifier has the advantage of high efficiency over a wide output range. Efficiency ranges from 65 to 85 per cent depending on the type of circuit and load; it remains practically constant from 20 per cent to 140 per cent of load, but below 20 per cent it falls rapidly. The best efficiency is obtained by operating the rectifier at as near full voltage as practicable. Unlike ordinary resistances selenium rectifiers have a negative coefficient of resistance, so that as the plate temperature rises the forward resistance decreases, thereby producing less heat.

The reverse resistance has no effect except heating in most circuits, although in the case of half-wave circuits (seldom used in plating practice) the output voltage across the load is influenced by the effect of the reverse current.

The rectifier plates are assembled on an insulated centre bolt with spacing washers and contactors interposed between the plates, as many as 40 plates being assembled into one element. Normally rectifiers are rated at about 0.16 amp. per sq. in. at 35° C. ambient temperature, although by wide spacing and the use of fins this can

be increased to 0.4 amp. per sq. in. The number of plates used depends on the voltage, the type of circuit and the current, but the size of the plate is governed by the current. Although, of course, excessive voltage and current are undesirable, the selenium rectifier will withstand high over-voltage and current for short periods without damage.

The output of a selenium rectifier decreases from 5 to 10 per cent at normal rating usually after 10,000–20,000 hours of continuous service. This ageing factor must be allowed for in considering the output of an installation.

Cooling. — The permissible temperature rise in the case of the selenium rectifier is higher than with the copper oxide type, so that it is possible to operate selenium rectifiers totally immersed in oil, using air-cooling tubes for the oil similar to those employed in the case of large transformers. Sometimes the oil is cooled by continuously circulating water in tubes through the oil tank containing the rectifier elements, but this is less reliable than the first-named method. It has, however, the advantage of conserving space and reducing the ventilating problem. Water-cooling is by means of copper coils in the top oil of both rectifier and transformer tanks, the water being circulated continuously. Water-failure alarms are included. Owing to the fact that the selenium rectifier is totally immersed, there is no difficulty that can be caused by the ingress of dust or by atmospheric corrosion. These units can therefore be mounted anywhere alongside the plating tank if desired — so that a minimum of bus-bar runs is required. It is this feature which constitutes the major advantage of the selenium rectifier over its copper oxide counterpart for plating purposes.

The main limitation to the current-carrying capacity of a rectifier



Fig. 63. 8-volt, 1,000 amp. selenium oil-cooled rectifier, with two tapping switches on the tank lid providing eleven steps of "on load" control and one off position

[Courtesy of Westinghouse Brake & Signal Co. Ltd.]

is the temperature rise; with the selenium type, so long as the oil temperature does not exceed 55° C. no trouble will be experienced. Thus, a greater overload can be taken in cold than in warm atmospheres, or when the rectifier is only operating for relatively short periods of time. Overheating can occur if the current taken from the rectifier exceeds the rated figure for any length of time; momentary short circuits do no damage. It is customary to provide overload protection on the A.C. side of the rectifier only by some such means as an overload relay connected to the current transformer to operate an alarm or to open the main contactor and so shut down the set. Alternatively, the relay can be arranged to operate if the D.C. current should change appreciably during plating.

Constant voltage control is sometimes used to increase the uniformity of plating and is helpful if the area of work in the tank does not alter greatly. This can be achieved by the means of a voltage relay which controls the drive to a motorised regulator should the voltage depart from the desired limits, or by means of a saturable choke circuit; the latter system is costly and is therefore only employed on low outputs. The system of voltage control has the limitation that it will not compensate for changes in solution characteristics, temperature or anode spacing. Fig. 63 depicts an 8-volt 1,000-amp. rectifier; two tapping switches can be seen on the tank lid which provide eleven steps of "on-load" control and one off position. The unit is oil-cooled; the internal arrangements are illustrated in Fig. 64, which shows a similar rectifier with the cover removed.

Recent Developments.—It is now common practice to install the main transformer, metal rectifier and control switches in a single natural-cooled oil tank. It is also possible to fit an "alarm unit" in which visual and or audible warning is given if the current in the plating bath diverges from within predetermined limits. The advantages of such a system where unskilled labour is concerned, especially on automatic plants, are considerable. Stand-by rectifier equipment is also now available. The half-wave characteristic of metal rectification is employed to switch accumulators statically into action if current failure should occur. At the same time the accumulators are automatically maintained in a charged condition from the power rectifier.

Automatic Current density Control.—The desirability of automatically controlling current density, particularly on automatic plants where a variety of articles are continually passing through is obvious. The difficulties of doing this are not readily overcome under all conditions, but a near approach to a solution to the problem has been

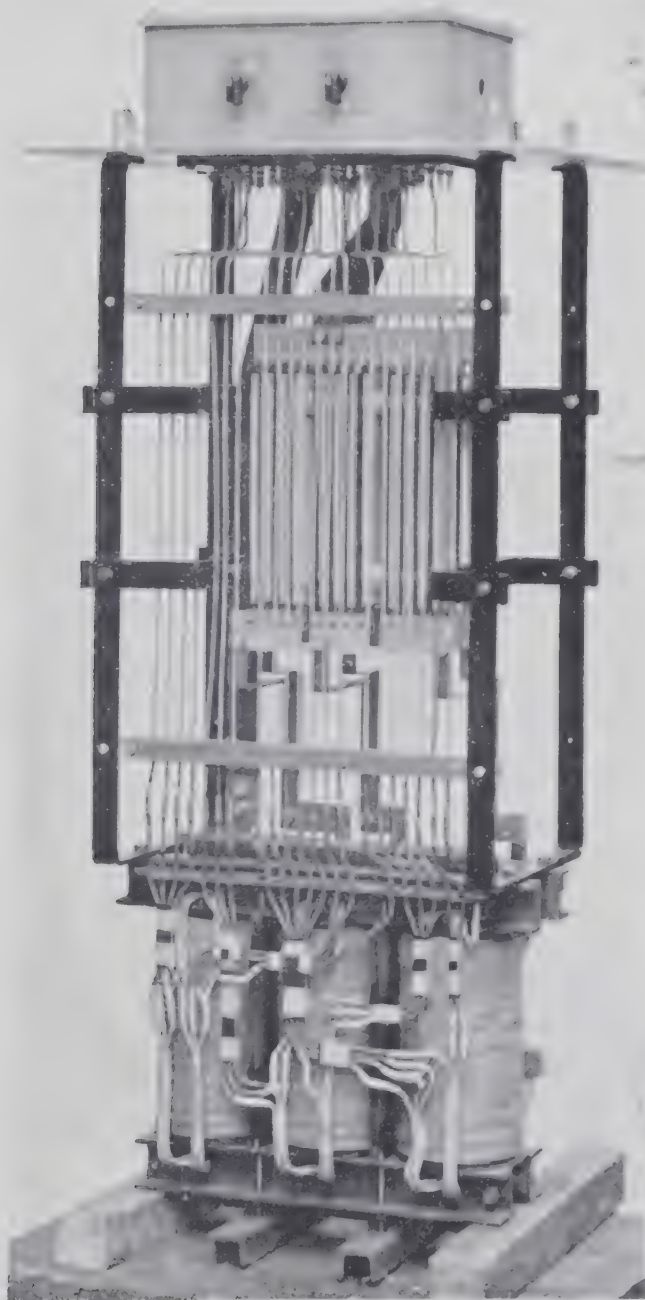


Fig. 64.—Selenium rectifier similar to that shown in Fig. 63, with casing removed to illustrate internal arrangement

[Courtesy of Westinghouse Brake & Signal Co. Ltd.]

described by Ashby.⁽³⁾ If the current and voltage at a bath for satisfactory deposition for varying areas of work are plotted, it will be seen that the points lie on a straight line, which when extrapolated cuts the zero current line at a positive voltage and has a definite upward slope. If a rectifier can be automatically controlled to operate at all times on this voltage-current line, the bath should operate at

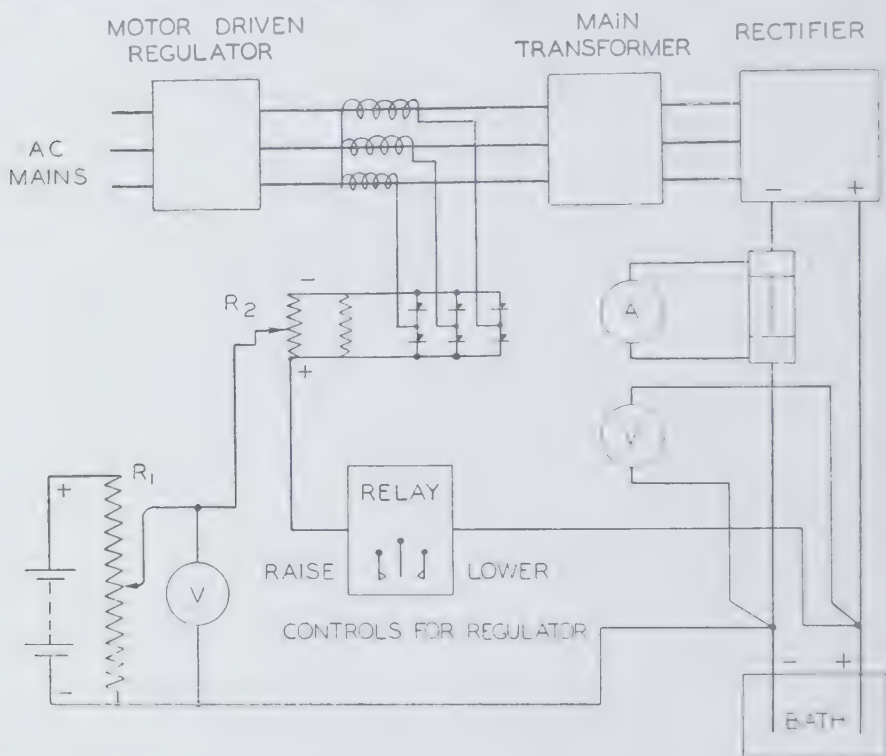


Fig. 65.—Basic circuit of C.D. control unit

constant current density, regardless of the load in the tank, provided the resistivity of the solution does not vary or the anode-cathode distance does not change excessively.

This has been achieved by an automatic apparatus consisting essentially of a dry battery across which is connected a potentiometer which is adjustable to control the voltage at zero current. A current transformer is connected in the A.C. lead from the regulator to the main transformer of the rectifier supplying the bath, so that the secondary current is therefore proportional to the D.C. current and is employed to control the slope of the voltage-current line by rectifying the output of the current transformer and feeding it into a potentiometer, part of the voltage drop across which can be connected in series with the dry battery to establish the reference voltage at which the bath should

be operating. The rectifier voltage is controlled by means of a relay between the reference voltage and the bath, the relay making contact on one side or the other, depending on whether the bath voltage is higher or lower than the reference voltage.



Fig. 66.—Modern type of resistance board, using expanded metal resistor elements

[Courtesy of W. Canning & Co, Ltd.]

In using the apparatus three or four values of voltage and current at which satisfactory plating can be carried out must be established for different areas of work so that the voltage-current line can be drawn. The voltage at zero current is fixed by means of the potentiometer, and the other potentiometer controlling the slope of the line is turned to the zero boost position. The rectifier will now adjust itself to deliver a voltage which will be on the predetermined line to within limits of ± 0.5 volt.

The load on the dry battery is only a few milliamps, so that it will last a considerable time. Fig. 65 shows the basic circuit diagram of the automatic control system.

Rheostats.—When a generator is installed in a plating plant it usually serves several tanks so that individual control of the current supply to each tank is necessary. This is most commonly carried

out by means of rheostats attached to each plating tank. Large current-carrying capacities are required in such rheostats so that the resistance coils are usually constructed of iron wire. The best types of resistance boards have coils of gradually increasing resistance values mounted in parallel. As the control switch is moved to increase the current to the plating tank successive coils are taken into circuit in parallel so that close control of the plating current can be obtained. To each board a voltmeter and an ammeter are fitted, these instruments being essential for successful electro-plating. Where large currents are employed, the ammeters are usually of the shunt type, so that only a portion of the main current need pass through the instrument, thereby reducing the dimensions of the latter. Fig. 66 shows a modern type of resistance board in which the resistances are of expanded iron construction. These are more robust than coil resistances. The actual construction of the resistor element is seen in Fig. 67.

Resistances are wasteful of current, and their use should be cut down to a minimum. With separate controlled rectifier units, it is possible, as has already been pointed out, to eliminate the need for rheostats entirely with substantial economies in current consumption.

HEATING OF SOLUTIONS

Many plating solutions must be operated at fairly warm temperatures, usually of the order of 100° F. to 160° F. The methods of heating adopted vary with the nature of the solution and the sources of heat available. Steam-heating is the most convenient for

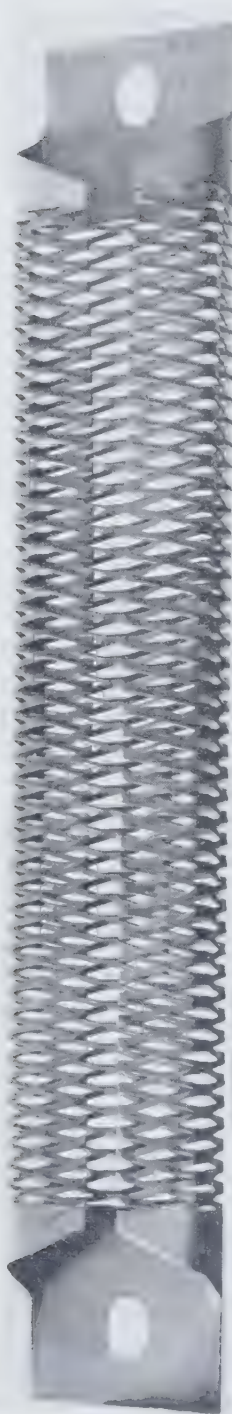


Fig. 67.—Construction of expanded metal resistor element

Courtesy of W. Canning & Co. Ltd.

many purposes if steam be available at a suitable pressure (about 40 to 60 lb./sq. in.). Lower pressures can be employed, but it is more economical to work with higher pressures, since coil and pipe dimensions are reduced for a given input of heat. Coils must be

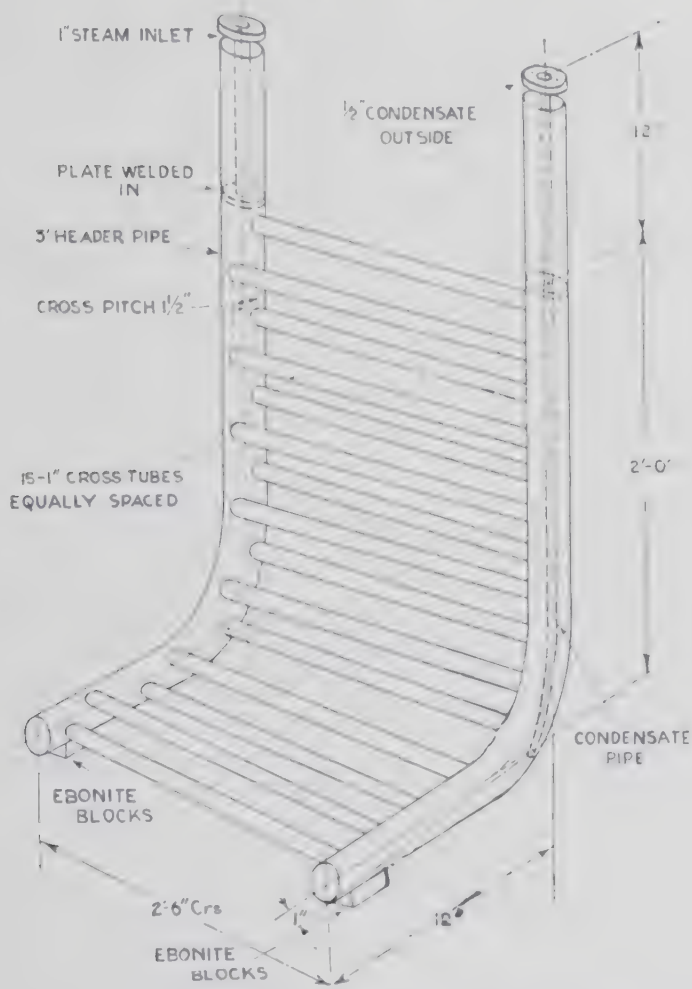


Fig. 68.—Steam-heating coil covered with hard rubber
[Courtesy of Nordac Ltd.]

employed; for nickel-plating solutions, lead-covered coils have been found satisfactory, while iron coils can be used in cyanide solutions. For bright nickel-plating it is desirable, if possible, to keep lead out of the solution altogether, and here hard rubber-covered steel coils have found useful application. The rubber covering has a considerably lower heat transfer coefficient than has lead, so that the heating surface has to be correspondingly greater. An example of a

steam-heating unit, in which, twin steel pipes are linked by a series of cross-tubes, is shown in Fig. 68. The entire assembly is covered with hard rubber to a thickness of $\frac{1}{32}$ in., and operates at a steam pressure of 60 lb. sq. in. Such heaters have given excellent service.

Solid nickel steam-heating units have also been designed for nickel solutions and used successfully. The steam enters the inner of two concentric nickel tubes mounted vertically in the solution, and leaves through an outlet in the larger outer tube. A series of such heating tubes is mounted together in a perforated ebonite cylinder which results in a thermo-syphonic heating effect; the ebonite also protects the heaters from accidental contact with work in the plating tank.

High-pressure hot water is employed in a similar manner to steam.

In the case of the corrosive and dense chromium-plating solutions, the usual procedure is to have the whole tank immersed in an outer water-jacket which is then heated by some suitable means, such as a steam coil.

Gas heating is often resorted to where this fuel is available, and can be carried out by means of injection burners and flue-pipes entering into the plating tank. An alternative method is to use a submerged cylinder made of a suitable metal in which a gas-air mixture burns, giving direct heating. This is especially useful in cyanide solutions where a steel cylinder can be safely used.

The modern tendency is to use thermostatically controlled external heat interchangers through which the solution is forced either by means of the pump used for filtration, or better, by means of a separate pumping unit. The interchanger is commonly a rubber-lined vessel with the heating medium circulating through tubes or coils of suitable material. Considerable success has recently been achieved by the use of heat interchangers made of high-silicon iron or of impervious graphite. The latter material can be employed as tubular or flat type heat interchangers, through which steam or high-pressure hot water are passed, the exteriors being corrugated to facilitate heat transfer. They can be used at pressures of up to 50 lb. sq. in., and have a higher transfer coefficient than that of steel.

Electric Heating.—Electric immersion heaters present a very flexible and convenient, if rather expensive, method of heating. The covering of the heater element must be suitably selected, a metal covering being most satisfactory. In actual practice electric immersion heaters have, on the whole, proved rather disappointing in

electro-plating. Metallic coverings tend to be corroded perhaps by stray currents, while the fixing head and the connections become badly attacked by spray and acid fumes resulting from their proximity to the solutions. Fused silica will withstand most plating solutions, and heating elements sheathed with this material have found some application. They suffer from the defect that the rate of heat transfer through the sheathing is poor.

Electric heating lends itself readily to thermostatic control, and immersion heaters incorporating an adjustable thermo-regulating device in the fixing head are available, and will give reasonable service under not too arduous conditions. Lead-covered units are commonly employed for nickel solutions, while steel-covered heaters are usually used with cyanides.

Agitation.—Agitation of plating solutions is carried out chiefly to enable higher current densities to be used. Nickel-plating is the outstanding case where the advantages of agitated solutions are most marked. The object of agitation is to secure relative movement between the solution and the articles being plated, so as to counteract the depletion of the solution with regard to metallic ions which takes place in the vicinity of the cathode under high-speed plating conditions. The same object may be achieved alternatively by imparting an oscillatory movement to the cathodes by a suitable mechanical device; this system is widely employed in the U.S.A. In this country, however, the latter method has attained no great measure of popularity for a variety of reasons, and agitation of the solutions by means of compressed air is generally resorted to. In automatic plants, agitation is often still required, since the rate of movement of the articles as they travel through the solution is inadequate. The air is introduced by a system of perforated pipes laid on the bottoms of the tanks, the source of supply being a compressor or a blower. Compressors are best avoided, since lubricating oil may be carried into the air-stream and find its way into the plating solution despite the best air filtering installations. Certain types of compressors are available, however, in which no lubrication is employed in the air chambers, and these prove very satisfactory, although their efficiency is rather low. Air-blowers, followed by water-washing of the air, provides an effective source of clean low-pressure air which is very suitable for the agitation of plating solutions. Recently, the use of ebonite agitation pipes has been introduced, and these are invaluable in almost every type of plating solution.

Air agitation should not be used in cyanide solutions owing to the oxidising effect of the air.

FILTRATION

The filtration of plating solutions, either continuously or periodically, is now recognised as essential in modern high-speed plating practice, especially where deposits of any appreciable thickness are being applied. The purpose of filtration is to remove foreign particles which find their way into the solution from the atmosphere, from anodes, from imperfectly cleaned work, and from other sources. Such impurities, if allowed to remain suspended in the solution, tend to become occluded in the deposits so that rough and porous coatings,

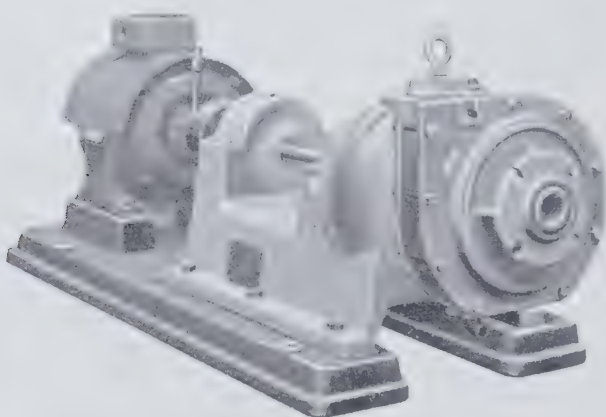


Fig. 69.—Mitchell-Shanks ceramic pump

[Courtesy of L. A. Mitchell Ltd.]

which are not only difficult to polish, but are of poor appearance and durability, are produced. A study of the advantages and limitations of the different types of filtration plants in current use has been made by Wernick and Silman.⁽⁴⁾

Pumps.—Whichever type of filtration plant is adopted, the solution is pumped through a filter bed under pressure by means of a suitable pump. Especially where continuous filtration is employed, the selection of a material for pump construction is not a simple matter; resistance of a metal to chemical attack by the solution used will not always guarantee its durability in service, since stray currents can cause severe attack of even the most highly corrosion-resistant metals. Centrifugal pumps constructed of Monel metal and solid nickel have had a limited measure of success in nickel-plating; high-silicon iron has been found to withstand the conditions better. The latter material has the disadvantage of being non-machineable, however,

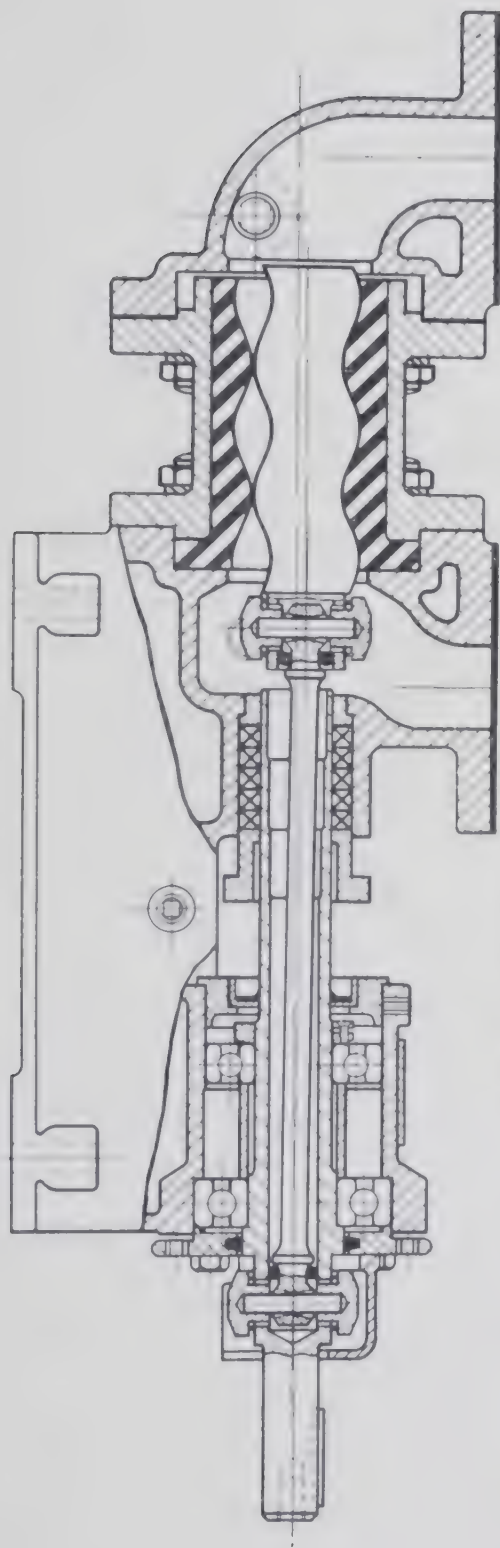


Fig. 70.—The "Mono" pump (diagrammatic section)

and casting, followed by grinding, has to be resorted to in the fabrication of parts made from it. High-silicon iron is a difficult alloy to produce, and disappointing results can be obtained if the material is not of a high standard of quality. The best solution to the pump question is to use a pump either made of a non-metallic material, or covered with an insulating coating, such as rubber. A number of excellent pumps of this description are now available. The Tungstone pump, for example, has an ebonite body and consists of two cylinders to which a motor-driven valve supplies air under pressure. The only moving part is a ball valve, and although the air is in contact with the surface of the solution it does not mix with it when the pump is operating correctly. A static head on the intake side is required and this can be obtained by immersing the pump on the bottom of the tank or installing it below the level of the tank floor. The Mitchell-Shanks pump is constructed entirely out of a hard, non-porous ceramic with an accurately ground impeller and body, the whole being armoured in a metal casing (Fig. 69). Laminated phenol formaldehyde resin-based materials have also been used in the manufacture of pumps for plating solutions (see p. 93), while an impeller pump constructed entirely of Pyrex glass has been marketed.

The *Mono* pump (Fig. 70) has found wide use for plating purposes also, because the only parts to come into contact with the solution are of rubber. A single rotor rolls in a fixed rubber stator which has the form of a double internal helix; the rotor is also of helical form but with a single scroll and with half the pitch of the stator. This means that the rotor maintains a constant seal across the stator and the two elements engage with one another in such a way that this seal travels continuously along the stator producing a uniform and positive displacement. The pump is self-priming with suction lifts of up to 25 ft., whilst the discharge is uniform and free from pulsation.

The LaBour pump (Fig. 71) is one which is particularly suited to the handling of plating and pickling solutions by virtue of its ingenious glandless sealing system. It is essentially a vertical self-priming impeller pump with an integral hydraulic seal. The drive shaft enters the pump on the suction side so that the seal only has to operate against atmospheric pressure and is independent of the discharge pressure. This seal consists of a "U" tube rotating in a horizontal plane about a vertical axis with the open end towards the axis and filled with the liquid being pumped. In this way a substantial force is set up, sufficient to maintain the seal which naturally only operates when the pump is running.

For use with nickel-plating solutions, it can be constructed from a corrosion-resistant alloy. A special high nickel-chromium alloy is available which resists almost every type of nickel solution.

The most important types of filter plant in large-scale use for electro-plating purposes are: (a) the filter-press; (b) the candle-type filter; (c) the pre-coated filter; (d) the disc-type filter; and (e) the centrifugal filter.

Filter Presses.—In its original form, the filter-press consists of a



Fig. 71.—LaBour pump

number of wood frames clamped together, over which fine filter cloth is stretched; this fabric acts as the filter medium, the liquid passing successively through the layers of filter cloth. More recently rubber-covered steel frames have been introduced, these being more durable and rigid than wood and less liable to contaminate the solution. In conjunction with a good pump, the filter-press is capable of giving a high rate of filtration; the cloth filter medium only gives a limited degree of clarification, however, while the labour involved in taking the plates apart for cleaning purposes and reassembling them is considerable. The construction of a modern filter-press for plating solutions is shown in Fig. 72.

Filter Candles.—In the candle-type of filter, the filtering medium consists of a number of cylindrical tubes made of fired

kieselguhr (a very finely divided diatomaceous earth consisting of practically pure silica), which are mounted in an outer container usually constructed of vitreous enamelled cast iron or of rubber-lined steel. These units are capable of giving very fine filtration, and particles as small as 0.0001 mm. in diameter can be removed. In time, the minute pores of the candles tend to clog up, however, so that increasing pressures become necessary if the rate of filtration is to be maintained. Kieselguhr candles are rather fragile and have in many instances been replaced by more durable candles of porous

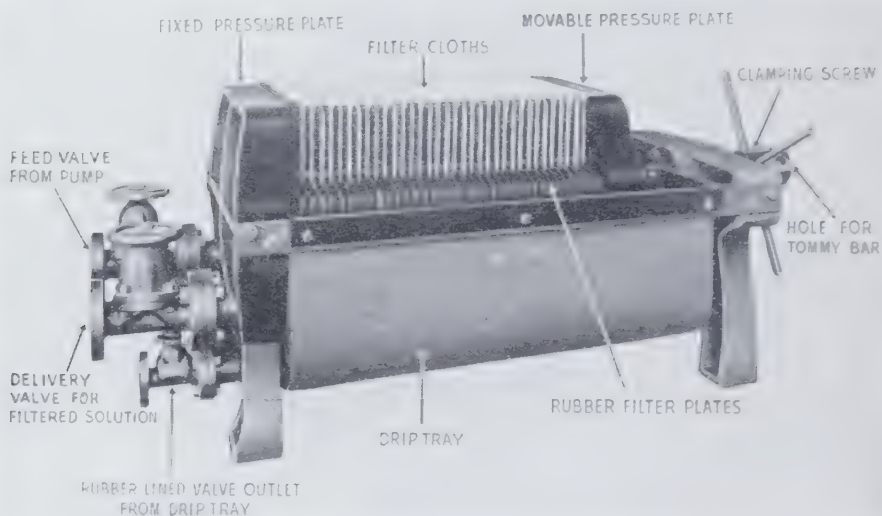


Fig. 72.—Filter-press for plating solutions

[Courtesy of W. Canning & Co. Ltd.]

stoneware which are available in varying grades of porosity; sludge can be removed from filter candles to some extent by applying a back-pressure of water. In all cases, however, candle filters have a limited life owing to the silting-up effect, which gradually renders them impermeable. Furthermore, the limited filter area obtainable with a unit of a reasonable size, and the labour involved in the frequent cleaning which is necessary militates against the extended application of this type of filter. Filter candles of porous ebonite have also been introduced, but they suffer from the same limitations.

Pre-coated Filters.—The best present-day filtration practice makes use of a renewable filter-bed on a suitable base. In principle the method consists in using a fairly coarse base material upon which a filtering bed of a suitable medium, e.g. a grade of kieselguhr powder, is built up. The method of preparing the filter-bed is to form a slurry in water or in a portion of the solution to be filtered

and to circulate this continuously by means of a pump until the filter medium has all been deposited on to the base to a depth of about $\frac{1}{8}$ in. to $\frac{1}{4}$ in. Filtration of the main bulk of the solution is then carried out in the normal manner until the rate of delivery falls too low. A small back-pressure of water is then applied, when the filter medium readily falls away from the base to the bottom of the container, whence it can be removed. The advantages of the pre-coated type of filter are very evident:

- (a) A large filter area can be employed with the result that only relatively low filtration pressures are required.
- (b) The filter can be easily cleaned and the filter-bed renewed without dismantling the unit; this makes for a minimum of labour in the maintenance of the filtration plant.

Filter candle units or even the filter-press can be used as a base on which to build up a filter-bed, and this method has in fact been employed. It results in a greatly increased life for the filter candles and makes for more easy cleaning, both in the case of candles and filter-presses. The main advantages of a renewable filter-bed are, however, obtained only when a large surface area of a highly porous base material is employed in specially designed units.

In one American type of unit several cypress wood or ebonite grids are mounted together inside a rubber-lined steel container; felt or cotton twill bags stretched over these provide the surface on which the filtering bed is built up, so that a considerable filtering area can be obtained in a relatively small unit. The only disadvantage of this type of plant is that the cloth used may introduce organic contaminants into sensitive solutions, but by the use of bags made of woven glass fibres even this can be obviated. The general arrangement of this type of filter is seen in Fig. 73.

In the Metafilter the base for the filter-bed consists of a large number of flat washers, generally made of stainless steel, having a series of scollops raised on one face standing about 0.001 in. to 0.002 in. above the general surface; these are assembled on a slotted supporting rod; the construction is shown in Fig. 74. The rings are designed so that a large contact area with a comparatively small flow space is obtained between successive rings; this is essential in order to prevent the kieselguhr from passing between the rings. The supporting rod and the retaining rings may be made of a variety of metals to withstand the particular solutions being used.

Disc-type Filters.—This type of filter makes use of a series of filter discs of suitable grades of compressed cellulose material which

are discarded and replaced by fresh ones when they become clogged with sludge. These filters have the advantage of eliminating the need for building up cakes of filter aid, whilst dismantling and cleaning are quickly and easily carried out, with little loss of solution. The fact that the filter discs can be obtained in a wide range of densities means also that the degree of filtration can always be under close control. These filters can be used in conjunction with activated carbon or other purifying agents if necessary.

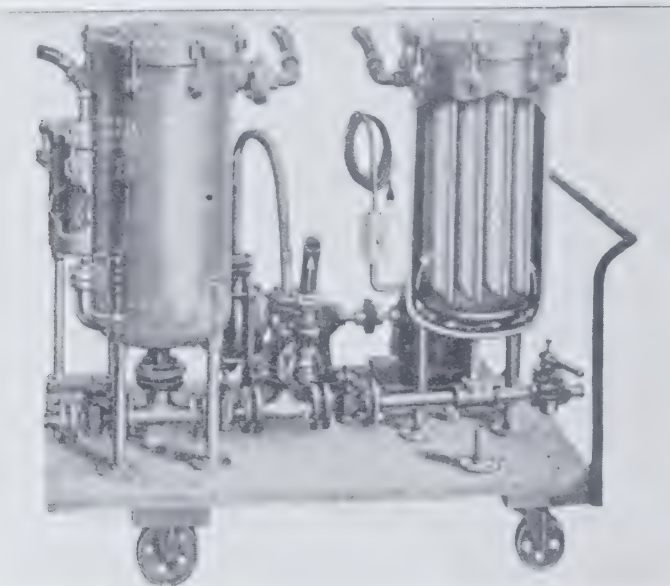


Fig. 73.—Filter unit. The assembly as illustrated has two filter units; each is a different type, both being mounted on one platform and operated from the same pump.

[Courtesy of Industrial Filter and Pump Mfg. Co., Chicago, U.S.A.]

The American "Alsop" filter is one of this type and consists of a number of units each made up of a sludge collecting ring on which is placed a cellulose filter disc followed by a perforated metal screen. A pile of these can units be built up over a central perforated outlet tube which collects the filtrate, the whole being contained in a cylindrical casing into which the solution to be filtered is forced by a suitable pump.

The liquid entering the cylinder passes through holes provided in each of the sludge rings. Half the liquid from each ring is then forced through the disc beneath it and half through the disc on the top of the ring, the sludge or sediment remaining with the ring.

The filtered liquid from each disc enters directly into the perforated screen next to it, and runs through the channels in the screen

to the common outlet screen in the centre. Each disc acts as an individual filter thus giving a large filtration area, whilst the entire surface of the disc is used effectively to collect sediment, as the pressure throughout the filter is uniform.

The "Sparkler" filter, also widely used in the United States, is

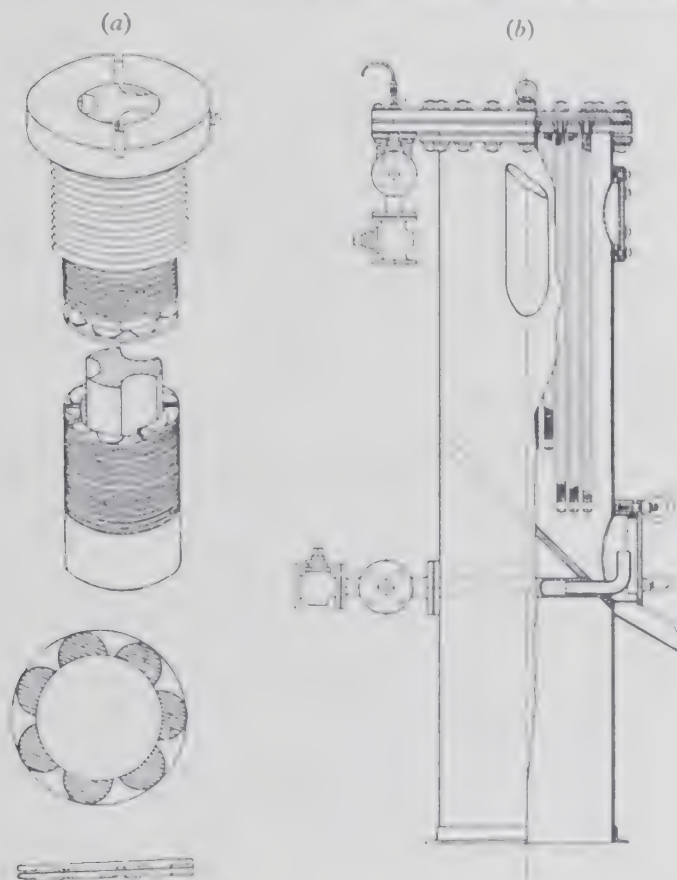


Fig. 74.—The Metafilter

- (a) Filter rings and support showing method of assembly
(b) Construction of the unit

similar in principle; the filter medium is either paper or cloth supported on horizontal perforated plates which may be of nickel, ebonite, steel, etc., depending on the solution. A series of these filter plates is built up, in an outer cylinder, each plate being separated from the next by a collecting plate leading to a central vertical outlet pipe. Filter aid or activated carbon can be used as a filter layer on the horizontal filter plate where it is held by gravity.

A horizontal plate filter which gives a high degree of filtration by making use of porous paper filter pads is the "British" filter. The

filter plates are on the combined plate and chamber principle. They are assembled on to a central bolt and interleaved with the filter mats. Continuous feed and drainage ports are made by coincident holes in the plates and mats. Any number of mats can be used, the larger the number of mats, the greater being the filtering area. The filter plates can be constructed of glass, but for use in a plating

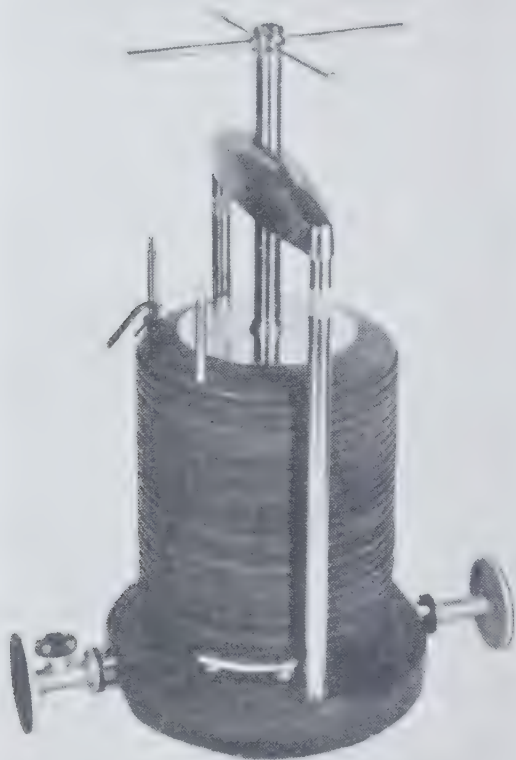


Fig. 75.—The "British" filter

[Courtesy of British Filters Ltd.]

shop it is more practical to have these of a laminated phenolic plastic material which has superior mechanical strength and resists the usual types of plating solutions adequately. The metal parts of the filter unit are best made from stainless steel. To reduce edge seepage of the solution through the porous filter mats and to improve the assembly of the unit, rubber rings are fitted between the plates. For strongly alkaline solutions which may attack paper filter mats, woven polyvinyl chloride mats can be used which, unlike the paper mats, can be washed and re-used. Fig. 75 shows a "British" filter as employed for plating solutions.

Centrifuges.—Centrifugal filters can give a high rate of filtration and are capable of removing very fine particles. They are not yet widely employed in plating practice because, being precision-made instruments, they are relatively costly and are not really suited for the removal of the heavy contamination which is liable to occur in some types of plating solutions.

AUTOMATIC PLATING PLANT

Perhaps the greatest advance in electro-plating technique in recent years has been the introduction of automatic plating plants of a size and diversity of types which has in many respects transformed the entire conception of plating as a process. In most automatic plating plants, the articles to be treated are suspended from cathode bars which travel continuously through a series of tanks in which the cycle of operations constituting the plating process is carried out. The entire sequence of processes comprising cleaning, pickling, and plating can be handled, the time in each tank being controlled by the period of travel. It is evident, however, that as there is a continuous transference of articles into and out of each tank, the required degree of control of current density and plating conditions can only be obtained if substantial numbers of articles of the same or similar type are being handled.

The automobile industry has been in the forefront in the use of automatic plating equipment because of the large numbers of identical components which are required in automobile manufacture. Plants of considerable size have been constructed in this country; examples are the plating of zinc alloy motor-car handles successively with copper, bright nickel, and chromium, also the bright nickel- and chromium-plating of brass motor-car headlamps and radiator shells, and the silver-plating of lamp reflectors.

The cycle industry has also made use of automatic plating plant on a large scale.

The design of an automatic plant for handling individual components demands a great deal of engineering skill owing to the multiplicity of factors involved. Current is supplied to the cathodes usually by means of sliding contacts at the ends of the work-carrying bars; these may be lifted out of each tank and lowered into the next by various devices, e.g. chain and sprocket mechanisms coupled with continuous conveyors to move the cathode bars slowly through each tank in succession. A plant of this type for the automatic bright nickel- and chromium-plating of cycle parts is shown in Fig. 75.

The "Duplex" Carriage.—In the Duplex carriage principle an

interesting method is used; two carriages run one below the other on the superstructure of the plant, chains attached to the upper carriage passing over pulleys on the lower carriage. Both carriages can move either independently or together; for lifting the carrier bars the upper carriage only moves forward, after which both carriages move simultaneously until the work is directly over the next tank in the sequence of operations. The upper carriage then moves backwards so that the work is lowered into the tank and is then moved forward by the continuous conveyor until the lifting mechanism comes into operation for the next transfer. A single electric

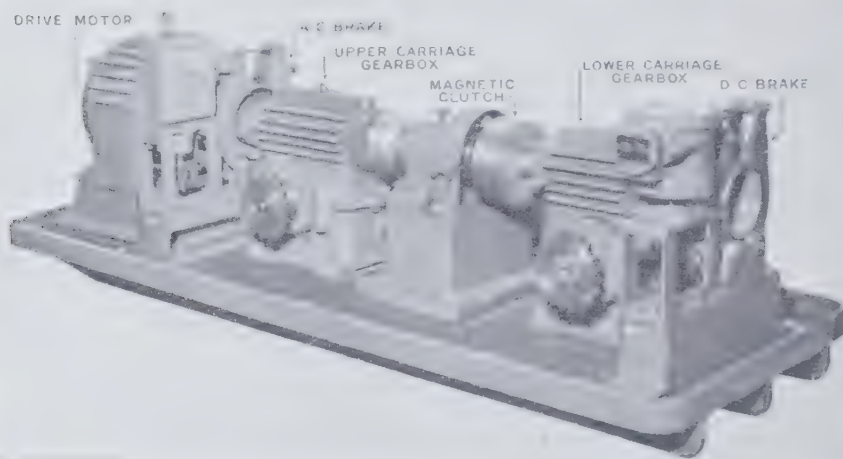


Fig 76.—Drive and gear-box mechanism for the Duplex carriage

motor is used for the drive, which is obtained through a worm reduction gear-box, first on the upper carriage and then through a further worm reduction box to the lower carriage. A single master controller works in conjunction with two rotary limit switches operated by the carriage drives, the circuit being arranged so that each movement is electrically interlocked. A timing device is also fitted to enable the cycle to be restarted after a variable predetermined period. The cycle is controlled by a system of limit switches, and the unit can be adapted to deal with the most complex cycle of operations. Fig. 76 shows the drive and gear-box of the controlling unit. Fig. 77 illustrates an automatic bright nickel- and chromium-plating plant for cycle parts operated on this principle. This plant is capable of plating seventy sets of cycle parts per hour (each set having a surface area of about 7 sq. ft.). The thickness of nickel deposited is approximately 0.0012 in. The rubber-lined steel

nickel-plating tank has a capacity of 6,000 gallons, the solution being maintained at its working temperature of 130 F. in an external rubber-lined tank, heated by means of nickel-plated Monel metal steam coils.

For small parts, such as nuts, bolts, washers, etc., automatic barrel-plating plants have been designed. Fig. 78 shows one such installation capable of zinc-plating some $1\frac{1}{2}$ to 2 tons of small parts per eight-



Fig. 77.—Automatic bright nickel- and chromium plating plant for cycle parts, employing the "Duplex carriage" transfer mechanism

Courtesy of the Electrochemical Engineering Co. Ltd.

hour day. The barrels are fitted with a pinion which engages with a worm at the side of each tank, thus enabling them to be rotated continuously while in the solution. The method of transfer of the barrels through the tanks is by the Duplex carriage system already described.

Side Arm Automatics.—The side arm principle has been employed for the design of automatic plating and pickling plant extensively in the United States and to a lesser extent in this country. In this design, which is especially suitable for the rotary type of plant, the plating racks are carried on curved cast aluminium arms

supported from a moving conveyor on one side of the plating tanks. Transfer from one tank to the next is obtained by means of a suitably designed stationary cam attached to a roller track against which the lower end of the overhanging carrier arm rests. The arm then rides up one side of the cam casting, across the flat section of the cam and down into the next tank. All the moving parts—conveyor chains, carrier arms, transfer cams, driving mechanism and cathode rails are mounted on the central chassis of the machine, so there is a complete absence of overhead construction, which makes for ready accessibility. The weakness of this design is, however, the strain on

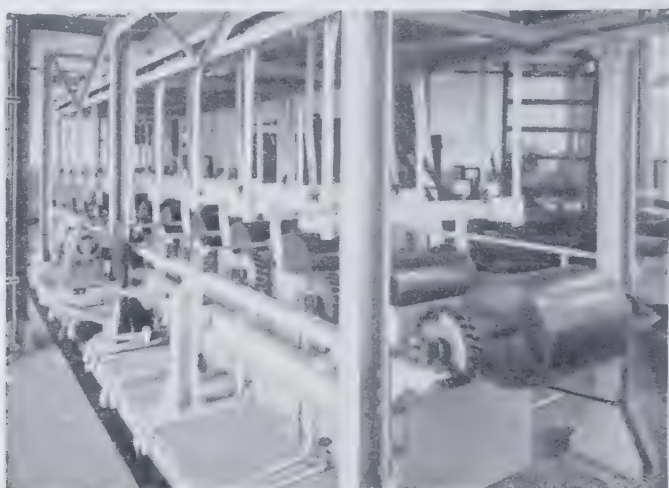


Fig. 78.—Automatic barrel-plating plant

[Courtesy of the Electrochemical Engineering Co. Ltd.]

the arms which may distort unless they are heavily constructed, whilst the speeding up which occurs at the ends of the plant may result in excessive swaying of the racks.

By the use of an auxiliary motor-driven cam the mechanism can be arranged to give a high degree of flexibility to the plant. Thus any plating time can be obtained without varying the transfer time, whilst particular tanks or operations can be omitted if required. Electrical control is provided for the motor driving the conveyor chain and also for the motor driving the transfer mechanism so that the chain is at rest when the lifting action takes place. This permits a vertical lift and eliminates swaying of the racks during the transfer. When the carrier arm has reached its highest position the chain starts to move until the rack has reached its set-down position. At this point the lifter lowers the rack in the next tank.

A wide variety of arm designs are available, and for the plating of articles of awkward shape bi-polar arms carrying auxiliary anodes can be employed.

The side arm principle has also been adapted for automatic barrel plating. Perforated plating barrels move in a vertical position at the loading end of the machine where they are manually filled. After loading, the plating barrel arm assembly which is attached to the conveyor chain travels over a stationary hump type cam to the first



Fig. 79.—Return-type automatic-plating plant

(Courtesy of the Electrochemical Engineering Co. Ltd.)

processing tank. As the barrel is lowered into the various tanks a bronze worm located on the spindle assembly between the plating barrel and the chain bracket meshes with a longitudinal steel worm and revolves the plating barrel continuously except during the actual transfer from one tank to another. At the end of the cycle the parts are automatically unloaded. Wide variations in the time cycle can be obtained with a constant transfer time and a variable period of rest or dwell. These machines are suitable for the treatment of bolts, nuts, screws, small stampings, etc.

Return-type Plants.—An essentially simple and very flexible type of fully automatic plating machine is shown in Fig. 79. The machine

is of the return type arranged so that the loading and unloading points are adjacent and only one operator is required. The racks carrying the work to be plated are carried directly on a single cathode track located centrally above the process tanks. At each traversing operation all the racks in the machine are moved forward one stage, the time taken for each rack to pass through the plant depending on the number of tanks and the time of treatment in each tank. This is variable, the normal rate of output being between 50 and 75 racks per hour.

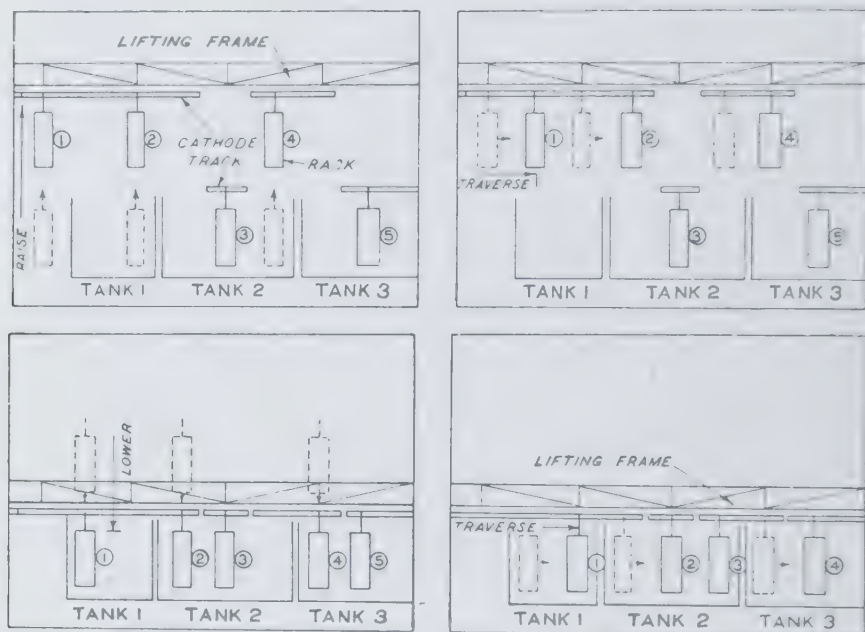


Fig. 80.—Method of rack transfer used in return-type automatic-plating plant shown in Fig. 79

The transfer mechanism consists essentially of a lifting frame incorporating a specially designed cathode rod from which the racks are suspended. A secondary mechanism moves all the racks in the machine laterally, this movement being synchronised with the raising and lowering of the racks on the lifting frame to effect the transfer. Racks in the plating tank and other multi-stage tanks are moved laterally only and remain immersed while the traversing operation is taking place.

The counter-balanced lifting frame is supported by chains passing over chain wheels mounted on a steel structure which runs the whole length of the machine between the process tanks. The illustration shows the lifting frame in the lowered position.

Drying of the work is effected by a hot-air dryer after the final hot-rinse tank which blows air through a heater unit by means of a centrifugal fan.

The method of transfer is shown diagrammatically in Fig. 80.

Another return-type plant is shown in Fig. 81. Here again there is a central lifting frame, but the work carriers move along a cathode track on the inner periphery of the tanks. Lifting of the frame is by means of arms, the mechanism being placed between the tanks. The

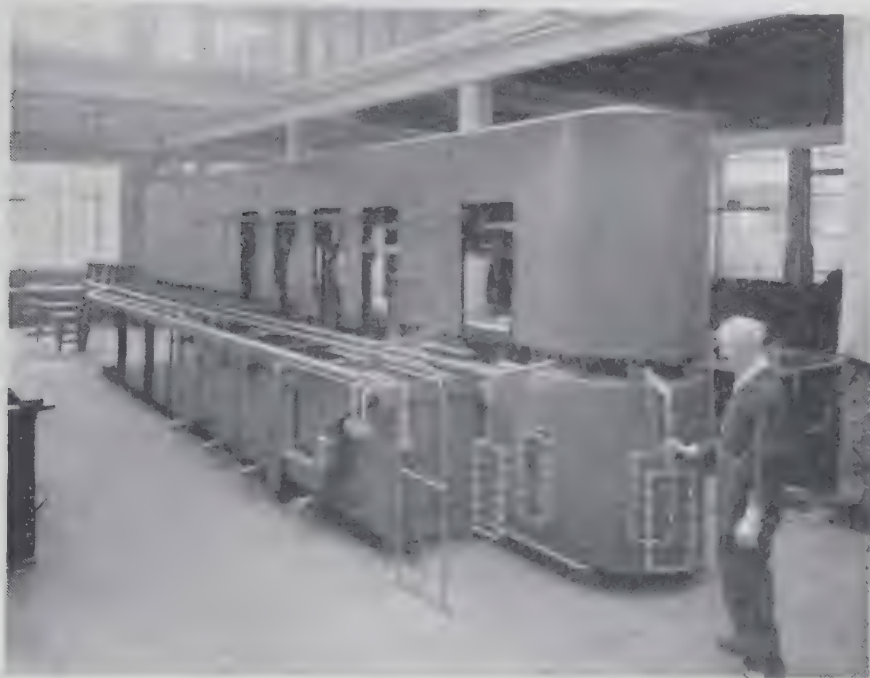


Fig. 81.—Automatic return-type plating plant

(Courtesy of W. Canning & Co. Ltd.)

use of a cathode track makes for a narrower lifting frame, but has the disadvantage of introducing an additional cathode track and carrier arms for the work.

A simple rotary type of plant for nickel-plating only and without transfer mechanism is shown in Fig. 82. A filter press installed on a truck for portability is seen in operation in the foreground.

Automatic Strip-plating.—Automatic plants have also become increasingly useful in the plating of metal sheet and strip. Here the design is different in that no lifting mechanism is required, the metal strip passing successively over a series of rollers from one tank to another. Nickel- and chromium-plated strip has been made in considerable quantities for a variety of purposes (such as for the

production of small pressed parts), while more recently large plants have been installed for the electro-tinning of steel strip to replace hot-tinned material. (See p. 370.) Continuous electro-galvanising plants for the manufacture of galvanised wire have also been successfully introduced (see p. 396) as have plants for the nickel-plating of steel wire for sealing through glass in the manufacture of electric-light bulbs. Narrow steel strip is plated continuously with zinc for the manufacture of flexible metallic tubing.

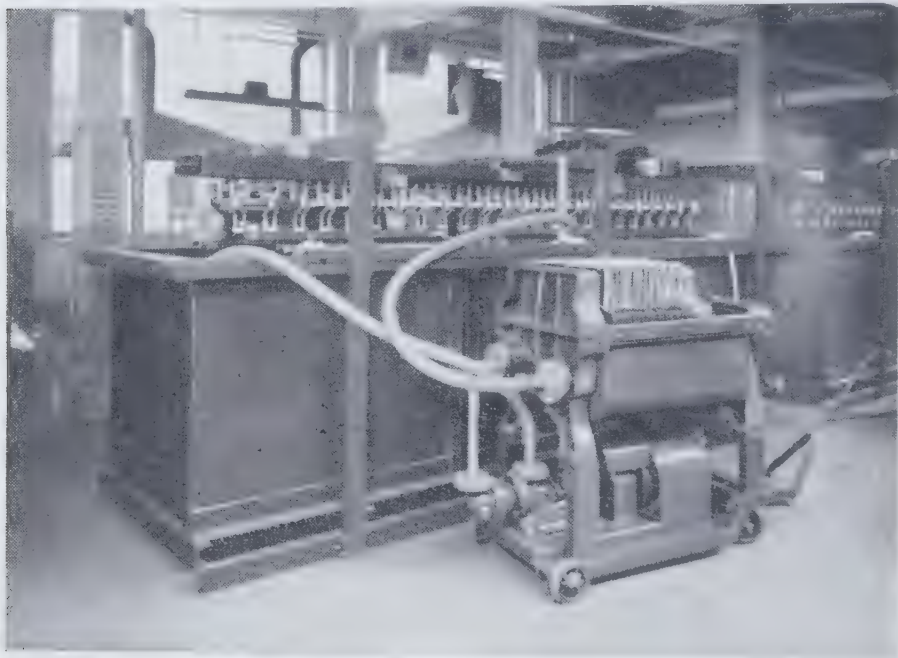


Fig. 82.—Rotary nickel-plating plant

[Courtesy of W. Canning & Co. Ltd.]

A diagrammatic lay-out of a continuous strip-plating plant for the bright nickel-plating of razor-blade strip is shown in Fig. 83. The plating tanks and heating coils are of rubber-lined steel, and the plant is capable of plating the equivalent of fifty blades per minute.

The number and diversity of automatic plants are tremendous, and further reference to some of these will be made when individual plating processes are being discussed.

Ancillary Equipment.—In up-to-date plating installations every effort is made to mechanise the control of processes and conditions as much as possible, so that there is a considerable emphasis nowadays on instrumentation as a means of eliminating the human element. Many of the items of equipment used in modern plating plants have already been referred to, i.e. filtration units, compressors, etc., but

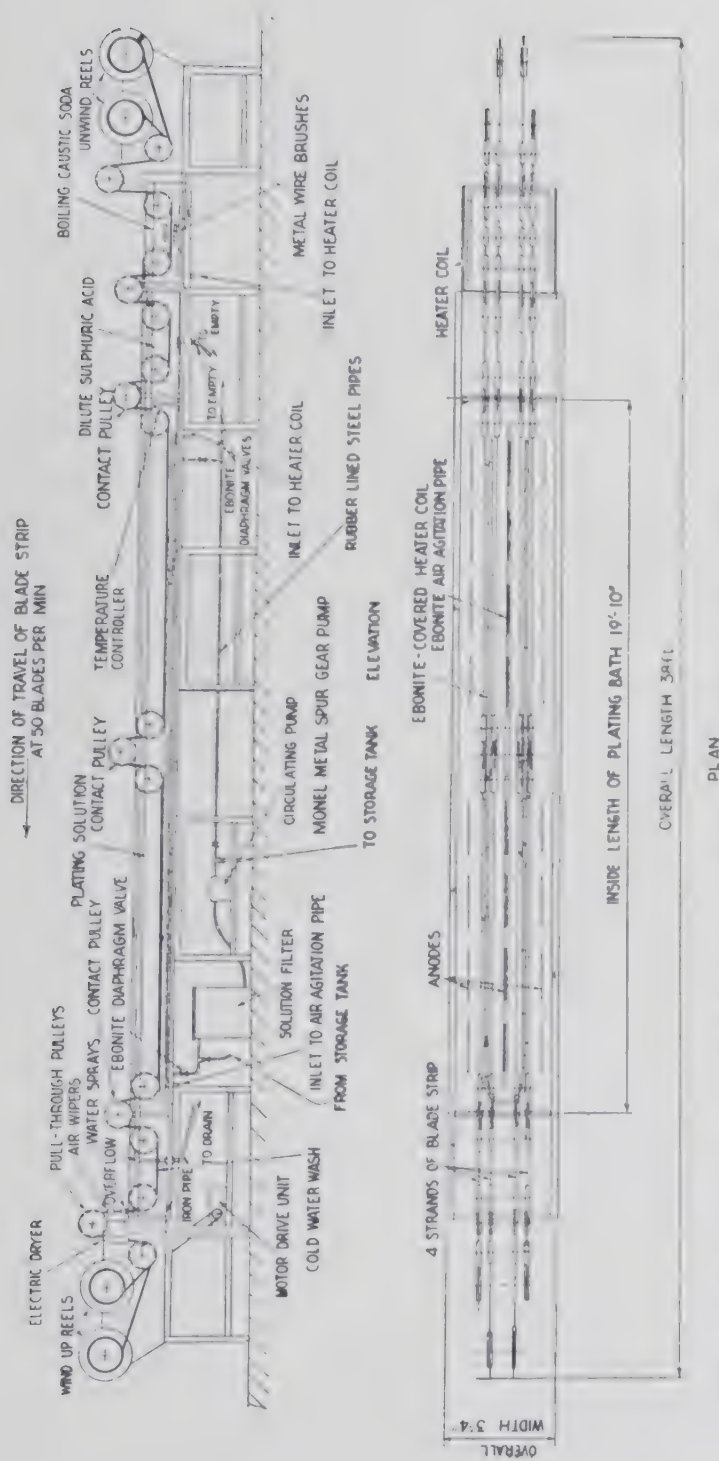


Fig. 83.—Diagrammatic lay-out of a continuous strip-plating plant for the bright nickel-plating of razor-blade strip
(Courtesy of Gillette Industries Ltd.)

a number of additional requirements are described below. There is also a very desirable tendency nowadays to mount indicating and control instruments on a control panel. This enables all the conditions under which the plating operations are carried out to be seen at a glance.

Thermostatic control of plating solution temperatures is commonly employed and has many obvious advantages. Temperature recorders are also often fitted, while dial thermometers remotely mounted from tanks are almost essential.

pH Control.—In nickel-plating especially the pH of the plating solution is important, and recording pH meters have been installed on a number of plants. It is possible also to control pH as well as record, but this refinement has, however, not yet received any wide practical application.

Current Control.—The ammeter and voltmeter are essential instruments in the control of plating processes. Ampere-hour meters, although much less frequently installed, are also helpful in plating to a specification, and can be linked up with a warning light or bell system to indicate when the required thickness of deposit has been applied.

Bus-bars.—Bus-bars for carrying current are usually of copper strip which must be of adequate section. Aluminium bus-bars have been used to a limited extent, but the metal is rather more corrodible than copper in plating shop atmospheres, whilst the resistance at junctions tends to become high during service.

Ventilation.—Exhausts to remove steam and fumes are very desirable and in many cases essential in a plating plant, especially on automatic equipment. Not only are the working conditions improved by the removal of fumes, but the structure and mechanism of the plant itself do not deteriorate nearly as quickly as when they are required to work in a poor atmosphere. Exhaust ducts should be of the slot cross-ventilation type, and may be of timber, or better still, of rubber-lined steel; the latter method of fabrication permits of great flexibility in design. It is nowadays the practice to exhaust not only acid fume producing tanks, but also alkaline tanks and all hot solutions evolving steam. This provides good working conditions and at the same time conserves the factory structure and equipment, reducing maintenance costs.

Alkaline tanks operate at 140° F. to 180° F. and need an extraction rate of at least 200 cu. ft. of air per minute per sq. ft. of open tank surface. Slot type hoods are most satisfactory and should be of adequate height to cover racks or baskets being transferred from one

tank to another. Acid dip tanks should be similarly treated, as should hot-water rinses.

Chromium-plating tanks need special attention to remove chromic acid spray in accordance with legal requirements. Tanks wider than 20 in. should have two slots along each of the longer sides of the vat, and a minimum air velocity of 2,000 ft. per minute at the slot should be maintained.

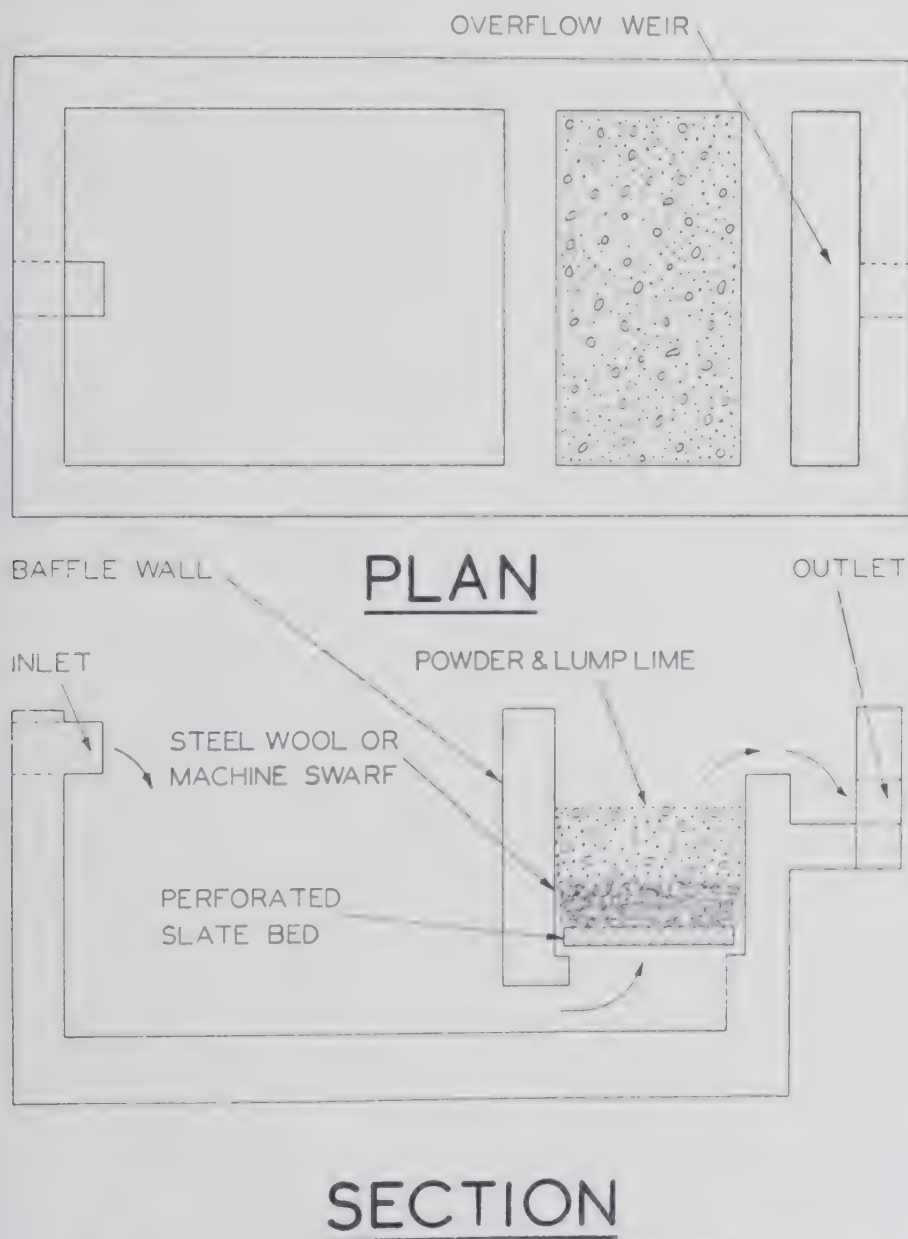


Fig. 84. —Lay-out of neutralising chamber for plating shop effluents

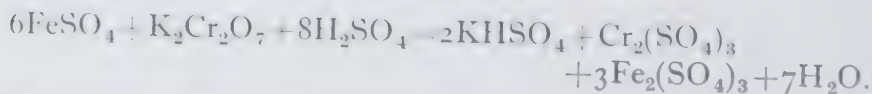
High-speed fans of the induced draught type are most satisfactory and may be rubber or plastic covered to protect blades from corrosion.

In the design of exhaust equipment adequate provision must be made for air input to enable the system to operate well. The location of air intakes must also be carefully decided upon, and the air may be filtered or pre-heated as desired.

Spare Tanks.—Adequate pumping and spare tank facilities should be provided to permit the speedy emptying of tanks for cleaning purposes or to enable the chemical treatment of solutions for the removal of impurities to be carried out.

Drains and Floors.—The flooring of a plating shop demands careful attention owing to the corrosive nature of the solutions. Blue-brick flooring with acid-resisting cement joints is satisfactory, but duck-boarding, formerly almost inevitably found in plating shops, is not really necessary provided the floor slopes adequately and drainage facilities are available. Where highly acid solutions are being handled (e.g. chromium-plating), neutralising chambers are often needed to deal with effluents.

Effluent Disposal.—In the installation of plant, proper attention must be given to dealing with effluents before they can be discharged to the public drains. Acid pickling solutions have already been dealt with (see p. 66), but plating operations involve the need for disposing of other noxious materials. A neutralising chamber containing lime is sufficient to precipitate simple metallic salts of such metals as iron, copper, nickel and zinc and to neutralise a reasonable degree of acidity provided a sufficient time of contact is allowed to raise the pH of the treated liquid to between 8 and 9. A typical arrangement is shown in Fig. 84. If chromates or cyanides are present, however, more elaborate methods are needed. A relatively simple method in the case of chromate-containing effluents is to treat the liquor with ferrous sulphate to reduce the chromates to the trivalent state after which milk of lime is added to precipitate the chromium and other metals. About twice the theoretical quantity of ferrous sulphate is recommended,⁽⁵⁾ and reduction is complete in about one hour at a pH range of 4 to 10. The reaction is as follows:



The process is essentially simple, although a considerable amount of sludge is produced.

The removal of cyanides is a more difficult matter. The cyanides can be destroyed by the addition of acid followed by aeration to

remove hydrocyanic acid gas, but the process is regarded as dangerous in view of the toxicity of this gas. An alternative method is the ferrous sulphate and lime treatment which in the presence of air leads to the precipitation of the cyanide in the form of blue complex cyanides of iron. The cyanide effluent should be treated separately from other waste waters to avoid the unfavourable effects of dilution and interference by other metals such as nickel.⁽⁶⁾ Solutions of cyanides containing more than 30 parts HCN per million could be reduced to about 5 parts per million by treatment with 15 to 20 lb. of ferrous sulphate crystals per lb. of cyanide (as HCN) at pH values of between 7.5 and 9. Such treated effluent is suitable for discharge to sewers. The complete removal of cyanides demands rather more elaborate methods of treatment.

PLATING RACKS

The design and construction of jigs and racks for supporting and holding articles during plating is a subject of great importance. In general, plating racks are necessary for large-scale production, although small articles are often suspended from copper wires. Racks are almost essential in automatic plants and the formation of uniform deposits is to a large extent dependent on good jigging arrangements. A metal of high electrical conductivity must be used for such jigs, and the section should be adequate for the current to be carried. Hard drawn brass is a most suitable material, whilst steel jigs are employed where greater strength is required. In the latter event allowance must be made for the lower electrical conductivity of the steel.

Fabrication must be by welding or brazing. Soldering or riveting are most unsatisfactory since connections made in this way soon work loose or become corroded.

Racks should be designed to provide the maximum capacity, coupled with the avoidance of shielding. The supports must also be located to facilitate the escape of gas from the articles being plated. Pocketing of gas will result in bare patches, whilst if the bubbles flow over significant surfaces rough or irregular deposits may result.

Rack tips and holders should be detachable if possible, and be arranged to give good drainage to avoid the retention of plating solutions, but must be of adequate dimensions to carry the current. Positive spring pressure is commonly required, but if the articles being plated are sufficiently heavy, gravity pressure may be adequate. For steel parts of suitable shape the use of racks having small magnets to act as work holders is often practicable.

Where sharp edges or points exist some shielding must be provided to prevent "burning" of the deposit. This is most conveniently done by making adjacent articles shield each other. In extreme cases, however, it may be necessary to provide special protecting strips, or "thievês", to overcome burning difficulties.

Racks should not be designed to allow articles to be too near the bottom of the plating tank; five or six inches of free space is desirable.

Most rack troubles in service are due to mechanical damage and adequate rack storage facilities should be provided.

Rack Insulation.—The covering of the non-contacting areas of plating racks with an insulating coating should be carried out wherever possible to avoid loss as a result of deposition of metal on to the racks; also proper insulation increases their life and results in more uniform plating. The problem of rack insulation has not yet been completely solved. A successful material must meet the following requirements:

- (a) It must not affect the plating solutions employed or be attacked by them.
- (b) It must not soften or weaken at the working temperature of the solution.
- (c) It must be a good insulator and be easily applied to complex-shaped articles to give a coating which is smooth and free from porosity.
- (d) It must be of adequate toughness and strength to resist mechanical damage in handling.

For many solutions (especially nickel) rubber-covered jigs have been found very satisfactory, although their initial cost is rather high. Soft rubber is not suitable in chromium baths, but ebonite will withstand such solutions well. Unfortunately ebonite is somewhat brittle, but grades of ebonite which are far more flexible and shock-resisting than the normal type can be produced by the use of certain synthetic rubbers (e.g. Neoprene). For nickel and chromium solutions cellulose varnishes are also satisfactory; in order to obtain adequate resistance to mechanical conditions it is, however, best to apply these varnishes after covering the racks with a suitable fabric tape. Chlorinated rubber lacquers have been employed with some measure of success, but the difficulty with many lacquers of this kind is that the coatings are too thin to withstand the severe handling which these jigs usually encounter, unless they are applied after taping.

Some of the newer synthetic resins are finding useful application, although with many of these materials adequate practical experience has yet to be obtained. Plasticised polyvinyl chloride resins and vinyl co-polymers have been employed on a considerable scale in the form of thick coatings applied from concentrated solutions in hot solvents by dipping, followed by stoving. The newest materials are, however, in the form of plastisols containing no solvents and harden by gelling of the vinyl compound on heating. Although the vinyl co-polymers go a long way towards meeting the requirements of good rack insulation their adhesion to metals is poor, and this is a serious drawback. Some degree of adhesion can be obtained by sand-blasting the plating racks prior to coating, or by the use of certain primers. The advent of certain materials of this group, e.g. polythene and the cellulose ethers in the form of tape and tubing, may provide new rack protectives for the plating industries. Polythene can be applied by flame spraying, but better results are obtained by coating the previously heated rack with polythene powder and then fusing with a flame.

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CHAPTER VII

ELECTRO-DEPOSITION OF THE PRECIOUS METALS

Of the metals of the platinum group, the only ones of interest so far as electro-deposition is concerned are rhodium, palladium, and platinum, of which the first is by far the most important.

RHODIUM-PLATING

Rhodium-plating has been found of value when a hard, non-tarnishing deposit of pleasing colour is required on silver or on silver-plate, gold, white gold alloys, and platinum. The metal can also be plated directly on to nickel. In the case of copper- or zinc-base alloys a nickel deposit should first be applied and should be of adequate thickness to protect the underlying metal from the action of the highly acid rhodium-plating solution.

Rhodium has very high resistance to corrosion and tarnish. It has also an exceptionally attractive appearance and is, therefore, very suitable for decorative plating. Rhodium-plating is now an established commercial process, but it is still a costly one. The high cost is due not only to the intrinsically expensive nature of the metal, but also to the difficulty of preparing a suitable electrolyte from which deposition can be carried out. This is inevitable in view of the immense resistance of rhodium to chemical attack.

Reflectivity.—The reflectivity of the metal is good (about 78 per cent), and this, coupled with its resistance to oxidation at high temperatures, makes it useful for the manufacture of reflectors where conditions are severe, e.g. cinematograph reflectors. Its hardness also makes rhodium-plated articles highly wear-resisting. The metal is widely used in jewellery, because its colour is more attractive than platinum. Rhodium-plated mountings are particularly pleasing when used for diamonds.

Apart from decorative applications, rhodium deposits have been employed for electrical contacts in highly corrosive atmospheres, and in radio work where the low contact resistance of rhodium junctions is invaluable.

A variety of processes has been described and patented at various times, but the only commercially successful baths are the acid solutions.

Solutions.—The plating solutions currently employed are: (a) solutions of rhodium sulphate, $\text{Rh}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$, containing 1 to 5 gm. of metallic rhodium per litre, together with some free sulphuric acid, and (b) phosphate baths with a similar metal concentration, together with a suitable concentration of free phosphoric acid. Of these baths the sulphate bath is the more important in this country.

The preparation and manipulation of the solutions is very difficult and demands considerable care.

The Sulphate Bath.—Rhodium sulphate can be produced by fusing the metal with potassium bisulphate;⁽¹⁾ the salt is extracted, dissolved in water, and caustic soda added to the warm solution until it is slightly alkaline. This results in the complete precipitation of the rhodium in the form of hydroxide. After washing, this precipitate is re-dissolved in sulphuric acid to produce a solution of the sulphate. A suitable method is to heat the hydroxide with the concentrated acid, using 4 c.c. of acid per gm. of rhodium metal present, until it has dissolved. The solution is then diluted to produce a plating bath containing some 2 gm. of metallic rhodium per litre, and filtered. The rhodium sulphate concentrate should always be added to a sulphuric acid solution in order to prevent the re-precipitation of the rhodium by hydrolysis. If precipitation occurs it is difficult to re-dissolve the hydroxide, and the bath may yield deposits of poor colour.

The bath consists essentially of an acid solution of rhodium sulphate, which is a well-defined salt having the composition $\text{Rh}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$.

The sulphate bath has been studied by Cinamon,⁽²⁾ who recommends the use of a solution containing about 1 gm. of rhodium metal per litre with 4 to 40 gm. per litre of sulphuric acid. The bath is operated at 80°C . At low temperatures bright deposits can only be obtained at current densities of 10 to 15 amps. per sq. ft., but at the higher temperatures current densities of up to 300 amps. per sq. ft. can be employed. The efficiency of the solution increases with increasing current density and metal concentration. Schumpelt⁽³⁾ recommends a sulphate solution containing 2 gm. per litre of rhodium metal and 20 c.c. per litre of sulphuric acid. The bath is operated at 40°C . to 45°C . with a current density of 10 to 100 amps. per sq. ft.

Most of the solutions actually employed are proprietary, and little information is available regarding the actual methods adopted for their manufacture or of their precise compositions. The rhodium

content of the solution is kept very low as compared with the concentrations employed in general plating practice in order to reduce both the capital cost of the bath and drag-out losses to a minimum. The actual cost of the metal is much higher than that of platinum, although this is to some degree offset by the substantially lower specific gravity of rhodium (12.4, as compared with 21.4 for platinum).

The solution is worked with insoluble platinum anodes and the metal content is replenished by the addition of the rhodium sulphate concentrate. Gold anodes may also be employed, but have not so far been used extensively. The solution must be operated in an acid-resisting tank. Stoneware is not suitable, as it tends to be attacked by the solution. Glass is very satisfactory for small tanks, whilst for larger baths hard rubber-lined steel gives good service. Heating can be carried out by electric immersion heaters with fused silica casings, or, alternatively, a water-jacket can be employed. The latter procedure has the advantage that the solution will not be lost if the container should fracture or develop a leak. The concentrated acid spray given off during deposition makes it desirable that provision be made for exhausting the plating tank.

The Phosphate Bath.—The phosphate bath can be prepared by heating the rhodium hydroxide solution, prepared as described above, with concentrated phosphoric acid, using 8 gm. of phosphoric acid per gm. of rhodium, subsequently diluting in the usual manner. A suitable bath would contain 2 gm. per litre of rhodium metal and 40 c.c. per litre of phosphoric acid (58 per cent), but the acid concentration is not critical. The phosphate solution does not consist of a single compound, but contains a series of complex phosphates of ill-defined composition. This may possibly account for the fact that the colour of rhodium as plated from a phosphate bath appears to vary with the concentration of metal in the solution. Generally, however, the colour is said to be rather whiter, and lacks the faint bluish light apparent in rhodium as plated from the sulphate solution. The bath is usually operated at lower temperatures than the sulphate solutions, i.e. at about 30°C. to 40°C.

The phosphate solution has a lower conductivity than the sulphate bath, so that higher working voltages are needed. Generally, however, the method of operation of the phosphate baths does not vary greatly from that used for the sulphate solution.

As to the relative merits of the two types of solution there is a considerable divergence of opinion. Both types of solution are, however, relatively simple to work and have good throwing power.

Deposit Thickness.—Rhodium is applied in the form of only very thin deposits, generally not more than one-millionth of an inch in thickness, although for specific applications (i.e. reflectors) deposits of four or five times this thickness may be used. If correctly applied, the deposit is fully bright and requires no buffing.

One-millionth of an inch of rhodium can be deposited in about one minute at a current density of 10 amps. per sq. ft. Rhodium deposits cannot normally be stripped if they are defective, owing to the fact that rhodium is insoluble in all acids which do not also attack the underlying metal. New deposits can, however, be directly applied over the rhodium without great difficulty. It is possible to remove rhodium deposits indirectly by anodic treatment in a 55° Be¹ sulphuric acid bath such as is used for stripping nickel deposits when the rhodium is plated over nickel, as is common. The temperature of the bath is 90° F. to 100° F. The stripping time is about an hour; dissolution of the nickel takes place through pores in the rhodium, and the rhodium itself falls to the bottom of the tank in flakes and may be salvaged.⁽⁴⁾

Platinum and Palladium.—Of the other metals of this group platinum and palladium deposits have attracted attention, but neither metal is as yet of any commercial importance in this field. Platinum can be plated from complex amino-phosphate baths⁽⁵⁾ or from diamino-nitrite solutions.⁽⁶⁾

Palladium is relatively low in cost, but the deposits are poor in colour. The most satisfactory baths are of the diamino-nitrite type. Palladium is characterised by its great capacity for absorbing hydrogen, and if much hydrogen liberation occurs at the cathode non-adherent dark-coloured deposits result.

GOLD-PLATING

Gold-plating is employed for tarnish resistance and for decorative purposes; articles of jewellery, the interiors of silver or silver-plated goblets and presentation cups, tableware, and musical instruments are regularly gilded.

In addition to this there are industrial applications of gold-plating, as in the protection of analytical weights and balance parts, for electrical contacts and for reflectors where especially high reflectivity in the infra-red region is required.

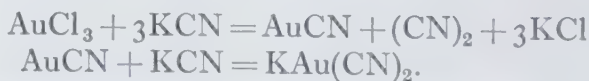
The principal solution used for gold-plating to-day is of the cyanide type. The bath consists essentially of a solution of the double cyanide of gold, together with a certain amount of free cyanide. The gold chloride bath, consisting of a solution of auric

chloride in hydrochloric acid, is also employed, but its throwing power is poor, whilst the deposit is larger grained and coarser than that obtained from the cyanide solution. In general, the chloride solution is, therefore, only recommended where heavy deposits of gold are required, as in the refining of the metal. Gold deposits are normally highly non-porous, so that they afford quite a good degree of protection despite the fact that they are almost invariably cathodic relative to the basis metal.

The treatment of metals prior to gold-plating is little different from that employed in the deposition of other metals. Adequate cleaning is essential, whilst scratch brushing is often resorted to.

Gold is often plated directly on to metals such as brass and copper, but this is to be avoided because of the low protection afforded to such metals by the thin gold deposit, and because there is some tendency for the gold to be absorbed. A nickel undercoat is greatly to be preferred. Soldered articles should be copper-plated before the nickel is applied.

The Cyanide Bath.—The cyanide gold bath is prepared by dissolving gold, in the form of chloride or cyanide, in a solution of sodium or potassium cyanide. Sodium cyanide is cheaper than potassium cyanide, and there seems to be little or no advantage in using the latter salt. When gold chloride is used for making up the bath, a precipitate of aurous cyanide is first formed on adding the cyanide to the chloride solution, and this dissolves in excess of cyanide to produce the double aurous cyanide:



The solution produced in this way contains potassium chloride. Although this is not generally considered deleterious, it is preferable to use gold cyanide, AuCN , for making up the solution, and this compound is now commercially available.

The free cyanide content of the bath need not be high; a minimum quantity is necessary to keep the gold anodes clean and bright, and to promote adequate anode corrosion; 2 to 5 gm. l. is usually sufficient. Carbonates build up in the solution with use and are, therefore, often not added to new baths. The presence of some carbonate is desirable to reduce fluctuations in the pH of the bath, although sodium phosphate additions have also been recommended for this purpose.

The metal content of the bath is kept relatively low in commercial practice to reduce drag-out losses. On the other hand, within limits, increased concentration of metal results in improved efficiency and

throwing power. The gold concentrations used are generally of the order of 1 to 5 gm./l.

Cyanide solutions are operated at fairly high temperatures (120° F. to 160° F.), the current densities employed being 1 to 5 amps. per sq. ft. Higher temperatures enable higher current densities to be employed, but in view of the thin deposits usually applied this is of no great consequence. Both the anode and cathode efficiencies approach 100 per cent under normal operating conditions.

Anodes.—Gold anodes tend to dissolve at too high a rate if they are used exclusively, and for this reason they may with advantage be replaced in part by insoluble anodes of carbon, platinum, or stainless steel. Alternatively, insoluble anodes may be introduced for short periods only from time to time when the gold concentration becomes too high.

When gold anodes are used their high rate of solution is due to the fact that the anode efficiency of the bath is about three times that of the cathode. Gold anodes also exhibit a tendency to become passive under certain conditions. Metallic impurities either in the anodes or the solutions tend to cause anode passivity, amongst these being lead, silver, bismuth or arsenic. The presence of sodium salts also promotes passivity, even if they are included in only small proportions.

Impurities.—Impurities, especially of the metallic type, must be kept out of the bath as they may adversely affect the colour of the deposit. Thus, silver and cadmium turn the deposit green, whilst nickel and zinc whiten it to some extent. Lead is especially deleterious, as its presence results in black, non-adherent deposits.

This effect is sometimes deliberately made use of in producing "coloured" gold deposits. These deposits contain only a very low percentage of the added elements, but their effect on the colour of the deposit is very marked. For *green gold*, silver cyanide may be added, whilst a small proportion of copper cyanide results in the deposition of *red gold*. *White gold* is deposited from a solution containing about 4 to 5 gm./l. of nickel (as cyanide).

Thickness of Deposit.—Gold deposits are usually very thin when applied for decorative purposes. Cheap articles of jewellery may carry as little as 0.000001 in. of gold, with deposits of 0.00001 to 0.00005 in. for better-class goods. For electrical contacts at least 0.0005 in. of gold should be applied.

In the deposition of gold Troy weights are commonly employed. Conversion factors are given in Appendix Table XIV.

Dip Gilding.—For the gilding of cheap articles and novelties, gold can be deposited by simple immersion in the gold solution. Brass and

copper are the most suitable base metals for such treatment, but if the gilding of other metals is required these may be coppered first.

In the "salt-water process" the gold solution is contained in a porous pot which is in turn suspended in a copper vessel containing sodium and ammonium chloride solutions in which a zinc plate is immersed. The solution is heated to about 70°C . On suspending the articles to be plated in the gold solution and connecting them to the zinc plate with a copper wire a primary cell is formed and gold is deposited without an external source of current. The deposits thus obtained are thin but very uniform. The process is subject to the disadvantage that the colour of the plate tends to become progressively darker in shade as the solution is used, so that it has to be discarded after a time, and the gold recovered by refining. This effect may be connected in some way with the build-up of copper in the solution, since 63 gm. of copper must dissolve for each 193 gm. of gold deposited.

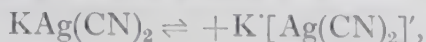
SILVER-PLATING

It is now over a hundred years since the first patent was granted to Elkington for silver-plating, this being the earliest patent covering the application of electro-deposited metal coatings for decorative purposes. The deposition of silver, although to a very large extent carried out on decorative tableware, musical instruments, and the like, has also found other applications, as in the silver-plating of electrical contacts, metal reflectors, and plant for the handling of food products where resistance to acids is required. Thin silver deposits are also applied to steel and other metals, and then treated with sulphide solutions and "relieved" to produce "oxidised silver" finishes. For cutlery and tableware the base metal used is most commonly nickel silver (an alloy of copper, nickel, and zinc) because of its white colour, and its suitability for direct silver-plating, but for some purposes, as in motor-car headlamp reflectors, brass is used, on to which an undercoat of nickel is applied prior to silver-plating; this improves the colour and wearing properties of the finished reflecting surface, and also enables good adhesion of the silver to be readily obtained.

Practically all commercial silver-plating is carried out using cyanide solutions which do not differ essentially from that originally developed by Elkington. A typical solution consists of:

Silver cyanide	.	.	.	40 gm./l.
Potassium cyanide	.	.	.	55 gm./l.
Potassium carbonate	.	.	.	35 gm./l.

This gives a solution with a "free" potassium cyanide content of about 35 gm./l. The solution is made initially by dissolving silver cyanide in an excess of a solution of potassium cyanide; occasionally silver chloride is used in the preparation of the bath, but it is best to use the cyanide. The silver then goes into solution in the form of the argento-cyanide, which ionises in solution:



the silver being in the complex anion. The anion is in turn very slightly dissociated:



As silver is deposited dissociation of the complex ion takes place further, the cyanide ions being discharged at the silver anode, forming more silver cyanide which dissolves in the plating solution. If the concentration of free cyanide is increased suppression of ionisation takes place, so that the concentration of silver ions is decreased; if it becomes excessively high deposition may be stopped altogether.

"Free" Cyanide.—The presence of "free" cyanide (i.e. cyanide in excess of that required to form the KAg(CN)_2 complex) and carbonate, within limits, improves the conductivity of the electrolyte and promotes regular anode dissolution. Potassium cyanide is preferred to the sodium salt in silver solutions, despite the lower cost of the latter, as there is less tendency for "burned" deposits to occur than with the sodium salt. If sodium cyanide is used, the carbonate concentration in particular must be kept low. Again, sodium carbonate, having a relatively small solubility at low temperatures, tends to crystallise out of the solution, especially in cold weather, causing trouble in plating, the small crystals attaching themselves to the cathodes, so that rough or pitted deposits result. Potassium salts are also generally considered in this country to favour the production of brighter deposits and to give plating solutions of high electrical conductivity. In the U.S.A., however, more use is made of sodium cyanide, and according to Sanigar⁽⁷⁾ there is no difference between the finishing characteristics or the appearance of deposits from solutions based on either sodium or on potassium cyanides. Excessive carbonate concentrations can be detrimental and can result in a lowering of anode and cathode efficiency. Carbonate can be removed by freezing or by treatment with calcium sulphate or calcium carbide. (See p. 382.)

Addition Agents.—The effects of various constituents and additions to the silver cyanide solution have been studied. Potassium salts, including the sulphate, carbonate, and nitrate, as has already

been stated, have been found to have a favourable influence on deposition, the corresponding sodium salts being in general much less satisfactory. Chlorides and sulphates markedly increase the hardness of the deposit.

Silver as deposited from a cyanide solution is dull and milky in appearance. The use of additives for the purpose of brightening the metal as deposited has therefore been extensively employed not only to minimise finishing costs, but also because the plating of a bright or semi-bright silver results in less removal of expensive metal in the actual polishing operation.

Under commercial conditions the most widely used brightening agent in silver-plating is carbon disulphide, which is added in the form of a dispersion made by shaking a small amount of the disulphide with a little of the plating solution and adding it to the rest of the bath. By the addition of the disulphide semi-bright deposits are obtained which are more easily polished; the proportion required is very small and should not exceed 1/100 fluid oz. per 100 gallons of solution. Solutions containing disulphide are, however, unsuited for plating on to soldered articles owing to their general inability to cover soldered areas. The addition of 1 gm. of sodium thiosulphate and 10 c.c. of ammonia per litre of solution has been advocated by Pan⁽⁸⁾ as giving better brightening than carbon disulphide. Many other addition agents have been tried, but without great success.

Egeberg and Promisel⁽⁹⁾ expressed the opinion that the brightening effect of carbon disulphide was due not to the presence of this compound, but to some reaction product of the disulphide with the solution. The effects of a range of possible reaction products, such as urea, thiourea, guanidine, and more complex compounds were examined. It was found that thiourea, in the proportion of 35 to 40 gm./l. gave a brightening effect superior to that obtained with disulphide, the optimum brightening being obtained within the current density range of 5 to 8 amps. per sq. ft. The thiourea remained stable in the solution for a considerable period. Active brightening effects were also obtained with urea, potassium thiocyanate, and thiosemicarbazide. Particularly good results were obtained with certain substituted dithiocarbamates, quantities of the order of 0.1 c.c. per litre having a marked brightening action. One such compound recommended has the composition:



Selenium appears to present some advantages as a brightening agent instead of sulphur. A patented high-speed silver-plating solution makes use of potassium selenite as the brightening agent.⁽¹⁰⁾

Other Solutions.—The advantages of a nitrate-containing bath have been pointed out by Promisel and Wood.⁽¹¹⁾ It is claimed that with the nitrate bath some of the anode corrosion is due to the nitrate ion, so that a lower range of free cyanide concentration can be used, even in the presence of carbonate, despite the known adverse effect of carbonate on anode corrosion. No carbonate is added to the solution to begin with, but the latter builds up as the bath is used. The nitrate solution consists of:

Silver (as metal)	.	.	.	16 to 18 gm./l.
Free sodium cyanide	.	.	.	15 to 22 gm./l.
Sodium carbonate	.	.	.	22 gm./l. (max.)
Potassium nitrate	.	.	.	113 to 150 gm./l.

The presence of potassium nitrate also has a favourable effect on the appearance of the deposit and higher current densities can be employed with a solution of equal silver concentration than in the absence of potassium nitrate. Sodium nitrate, on the other hand, is very undesirable in silver-plating solutions, and if sodium cyanide is used to supply the low concentration of cyanide required, the potassium nitrate concentration must be kept high relative to the total sodium ion concentration if the maximum advantage of the presence of the nitrate is to be obtained.

Other silver solutions not containing cyanides have been recommended from time to time, including sulphate, nitrate, and fluoborate baths. A complex iodide bath has been described⁽¹²⁾ in which a solution of silver iodide is made in potassium iodide, together with the addition of sulphuric acid, to produce a pH of 3 or less. Other acids (including organic acids) can be employed in place of sulphuric acid. The quality of the deposit is claimed to be as good as that obtained from the cyanide solution, and current efficiencies of 90 per cent are obtained. The process does not appear to have been applied commercially on any scale.

“Strike” Solutions.—On many metals silver has a tendency to deposit by immersion from a cyanide solution, which results in poor adhesion. This is particularly the case with brazed or soldered articles which are commonly silver-plated. For this reason, a “strike” solution is often used, prior to plating in the normal plating bath. This enables quick covering of the base metal to be obtained, after which plating is carried out as already described. Such “striking”

solutions have a relatively low silver ion content and are operated at high current densities. They may contain $\frac{1}{2}$ to 1 oz. of silver cyanide and 20 to 25 oz. of sodium cyanide per gallon of solution, but the precise composition depends on the type of work being plated, and must be determined by practical tests. The "strike" deposit must be sufficiently heavy to protect the underlying metal during subsequent plating, or unplated and thinly covered areas will result, while adhesion generally may also be poor. Very often, on brass, for instance, an undercoat of nickel can be applied prior to silver-plating; if the nickel deposit is satisfactory, the need for a strike deposit can be eliminated.

Alternatively, a momentary pre-dip in a weak solution of a mercury salt can be also used to improve adhesion of silver deposits on brass and copper. Such a solution is prepared by dissolving $\frac{1}{2}$ oz. of mercuric oxide in 1 gallon of water to which 3 oz. of sodium cyanide have been added. The mercury "quick", as it is called, is extensively employed and has the effect of protecting the base metal from oxidation before immersion in the silver bath; it also avoids the formation of an immersion deposit of silver on the base metal. This is because mercury is electro-negative to silver.

There is no simple analytical method of controlling the "quick" solution because of the interference of the other heavy metals which dissolve in it as the solution is used, so that most platers rely on the appearance of the mercury deposit as a guide to the working of the "quick". It appears, however, that most troubles with mercury "quicks" are due to excessive mercury content. The mercury content can fall to as little as $\frac{1}{10}$ oz. per gallon, and the solution will still function provided an adequate concentration of cyanide is maintained.

A preliminary copper "strike" from a cyanide copper-plating solution has also been found very useful and has received considerable application.

Plating Conditions.—Silver cyanide solutions are usually operated at room temperature, although it is desirable not to let the temperature drop too low in cold weather, to avoid crystallisation. On the other hand, excessively high temperatures cause cyanide decomposition and result in matt deposits, although, within reasonable limits, higher temperatures enable higher current densities to be employed; this, in turn, improves the "throwing power" of the solution. The optimum plating temperature appears to be in the region of 80° F. to 85° F.

Current densities are generally low, deposition being usually carried out at an average of 5 to 10 amps. per sq. ft., although

naturally considerably higher current densities are employed in "strike" solutions. Current densities of more than 15 amps. per sq. ft. are seldom used commercially, owing to the danger of burnt deposits. Moreover, the deposits applied are not usually very thick, and this, coupled with the high atomic weight of silver, means that the time of deposition need not be excessively long even at low current densities.

The silver metal concentration plays an important part in the feasibility of plating at higher current densities, although it is more expensive to work with solutions having greater metal contents because of their increased initial cost and high drag-out losses. Nicol⁽¹³⁾ recommends a concentration of 20.5 gm. l. of metal, and cites the effects of increased silver content on the maximum current density (Table XXXII).

TABLE XXXII

EFFECT OF SILVER CONTENT ON MAXIMUM CURRENT DENSITY
IN CYANIDE SOLUTIONS

Silver content		Maximum current density amps. sq. ft.
Troy oz. gall.	Gm. per litre	
3.00	20.5	6
4.00	27.3	7
5.00	34.2	8
6.00	41.0	10
7.00	47.8	10

Usually the anode and cathode efficiencies of silver solutions approach 100 per cent, although in "striking" solutions the cathode efficiency is somewhat lower. The cyanide solution has good throwing power, but covering may be poor on some metals, due to its low cathode polarisation. Apart from the effects of cathode polarisation, the conductivity of the solution has an important influence on the throwing power. Increased potassium carbonate concentration results in improved conductivity of the solution, while, on the other hand, higher free cyanide concentrations have the opposite effect.

Silver-plating solutions do not demand a great deal of filtration, but periodic filtering helps to avoid rough or pitted deposits. Metallic impurities do not appear to have any deleterious effect on the solutions, although high iron concentrations may result in yellowish

deposits. Pure silver anodes must be used since even small quantities of impurities in the metal may result in a black film forming on them. This film disintegrates, causing rough or pitted deposits to be produced. In some cases a high-temperature annealing treatment of silver anodes followed by quenching has been helpful in improving anode dissolution and in preventing the formation of anode films.

The anode and cathode areas should be approximately equal.

Lead-lined wood tanks with an inner matchboard lining have been



Fig. 85 (a).—Silver-plated reproductions of Old English and Sheffield plate
[Courtesy of National Jewellers' Association]

used very widely for silver-plating solutions; stoneware tanks have also been employed in small plants. Cathode bars are sometimes connected to a reciprocating mechanism which imparts a slight movement to the articles being plated; this results in improved deposits, the slight agitation helping to keep the solution uniform in composition and preventing striation.

Electro-polishing of Silver Plate.—Silver can be electro-polished by reverse current treatment in a cyanide plating solution. An alternating current is used with an anode current density of 30 to 200 amps. per sq. ft. The current must be sufficiently low to prevent gassing, and little or no metal is removed. A recommended plating and polishing solution contains 32 gm. l. silver, 40 gm. l. free potassium cyanide, 50 gm. l. potassium carbonate, and 10 gm. l. potassium hydroxide. The pH is 11.5.⁽¹⁴⁾

Applications.—Increasing use of silver deposits on non-ferrous alloys or even on steel is now being made for industrial purposes, especially for plants used in the food industries, and on electrical contacts. For cutlery, silver deposits are usually quoted in terms of the number of dwt. per doz. articles, and the qualities produced range from 10 dwt. per doz. for cheap cutlery to as high as 20 dwt. per doz. for high-grade hotel plate. Normal cutlery deposits range from 5 to 10 dwt. per sq. ft. of surface plated, although high-quality plate may



Fig. 85 (b).—A modern electro-plated cocktail shaker and modern luminous lamp with a frosted glass globe

[Courtesy of Adie Bros. Ltd. and National Jewellers' Association]

carry 20 dwt. per sq. ft., equivalent to a thickness of 0.00125 in. of silver.

In the case of good silver-plate an extra deposit is applied to points of maximum wear, such as the bowls of spoons. This is usually carried out as a separate operation by means of auxiliary anodes. Fig. 85 (a) shows silver-plated reproductions of old English and Sheffield plate, including dishes, candlesticks, sauce-boat and condiment sets. Fig. 85 (b) illustrates a modern electro-plated cocktail and modern hurricane lamp with a frosted glass globe.

Tarnishing of Silver.—Silver-plate tarnishes when exposed to the atmosphere, due to the formation of a black sulphide film. Rhodium-plating has recently become increasingly popular on

decorative silver-ware for this reason. The deposition of a hard film of beryllium oxide on to silver has also been described as a method for preventing the tarnishing of silver.⁽¹⁵⁾ The beryllium is deposited from a solution of 3.4 gm. l. of beryllium sulphate, $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$, adjusted by the addition of ammonia to a pH of 5.83 corresponding with the formation of the basic sulphate $\text{BeSO}_4 \cdot \text{Be}(\text{OH})_2$. A current density of 50 micro-amps. per sq. cm. is used, the time of treatment being fifteen minutes.

Attempts have been made to plate alloys of silver and cadmium or silver and lead, it being claimed that these have greater tarnish resistance than pure silver. Both of these alloying elements have the disadvantage of toxicity, however, and the processes have received little or no commercial application.

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NICKEL-PLATING

Nickel is one of the most important of the electro-deposited metals, and is unrivalled for its general usefulness as a coating for steel, brass, and zinc-base die-castings where decorative as well as protective properties are required. It is almost exclusively employed as an undercoating for chromium deposits on these base metals. Nickel, as plated, is normally dull in appearance (except in the case of very thin coatings), and is usually polished when it is to serve as an undercoat for chromium. By the use of special types of solutions it is possible, however, to obtain bright coatings which need little or no buffing. This relatively recent development is of great commercial importance and will be dealt with in detail later.

Cleaning before Plating.—As in all plating processes, metal surfaces must be thoroughly descaled and cleaned prior to plating, and may then have to be polished if a decorative finish is to be applied. The degree of finish of the base metal depends on the thickness of the nickel coat; thus, in the plating of motor-car bumper bars, where relatively heavy nickel coats are applied, only a medium polish is required, the final effect being achieved by polishing the nickel.

Good adhesion is most important, particularly where the nickel-plating is followed by chromium, because the stressed nature of the latter deposit tends to lift the underlying nickel. In the case of steel articles, cleaning in a hot alkaline solution followed by anodic "etching" in 10 to 70 per cent sulphuric acid for a minute or so is often resorted to prior to plating. Copper and brass are cleaned in alkaline solutions and may then be dipped in a weak cyanide solution followed by a dilute hydrochloric or sulphuric acid dip to remove tarnish. In the case of bronzes or where any appreciable amount of tin is present in the alloy the cyanide dip is best omitted as it may lead to poor adhesion. Thin copper undercoatings (about 0.0001 in.) are sometimes used on steel to minimise porosity and to increase the corrosion resistance of the deposit, but recent investigations have shown that little improvement results from such an undercoat which may tend, moreover, to reduce the adhesion of the nickel. The degree of finish of the basis metal and the absence of inclusions and defects has an important bearing on the durability of the nickel-plate.

Zinc-base die-castings require a special plating procedure (p. 292).

The Watts Bath.—With some exceptions, the Watts bath⁽¹⁾ is the mainstay of modern nickel-plating processes. It has undergone a number of changes since the original composition was suggested by Watts, but, fundamentally, it still consists of a solution of nickel sulphate containing some chloride and boric acid.

A typical bath, which is operated on a considerable industrial scale, consists of:

Nickel sulphate	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	.	.	48 oz./gall.
Nickel chloride	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	.	.	6 oz./gall.
Boric acid	H_3BO_3	.	.	3 oz./gall.

Operating Conditions—

Temperature	.	.	.	90° F. to 95° F.
pH	.	.	.	5.6 to 5.8
Current density	.	.	.	20 to 40 amps./sq. ft.

It is desirable to have a relatively high nickel sulphate content, together with agitation of the solution or movement of the work being plated, since it is under these conditions that it is best possible to maintain satisfactory rapid plating. Nickel ions have relatively low mobility and these steps prevent impoverishment of the solution in the neighbourhood of the cathode; where the shape of the articles results in heavy drag-out losses it may be necessary to effect a compromise by working with a solution of lower concentration on economic grounds.

Chlorides and Boric Acid.—The presence of chloride in the solution promotes anode corrosion; nickel anodes tend to become somewhat passive under certain conditions, and this is minimised by the presence of chlorides. Nickel chloride is to be preferred to sodium chloride, as there is some evidence that alkali metal ions are not a desirable ingredient of nickel-plating solutions; moreover, the nickel ions contributed by the former salt perform a useful function in the solution. Chlorides also appear to help cathode efficiency and the production of smooth deposits. These advantages have, indeed, recently led to the suggested use of a solution based entirely on nickel chloride. (See p. 291.)

Boric acid acts chiefly as a buffering agent and aids in the maintenance of the pH of the solution. Control of the pH value of nickel-plating solutions is essential and wide fluctuations are to be avoided. By the addition of boric acid, the tendency for rapid changes to occur is reduced. It is also said that the presence of this material

is conducive to the production of white, ductile, and smooth deposits.

"Double" Nickel Salts.—The "double nickel salt" bath which was at one time used almost exclusively for nickel-plating prior to the introduction of the Watts solution is essentially a solution of nickel ammonium sulphate; it has now been displaced by the nickel sulphate bath for practically all purposes. One of its chief disadvantages is the fact that the double salt has a low solubility, so that concentrated solutions which are necessary for high-speed plating cannot be used.

For barrel-plating this type of solution is, however, still widely employed in this country, because of the fine-grained deposit which it produces and the rapidity with which covering is obtained. A typical bath, as used to-day for barrel-plating, which contains an excess of nickel sulphate, consists of:

Nickel sulphate	.	.	.	12 oz./gall.
Ammonium sulphate	.	.	.	6 oz./gall.
Sodium chloride	.	.	.	2 oz./gall.
Boric acid	.	.	.	1 oz./gall.

The solution is operated at a pH of 5.6 to 5.8, and at room temperature. The current density employed is low, i.e. of the order of 6 to 8 amps. per sq. ft.

The presence of ammonium salts in the solution has a definite hardening influence on nickel deposits, quite small concentrations having a marked effect. This is taken advantage of when hard nickel deposits are required for wear resistance or for electrotypes; nickel having a Diamond Pyramid hardness of 400 to 450 can be obtained in this way, as compared with a figure of 140 to 160 for the usual soft nickel-plate.

Effect of pH.—Nickel solutions are operated at pH values ranging from as low as 1.5 to values in excess of 6. Too high pH values should not be employed or precipitation of basic compounds will occur. A pH range of 5.4 to 5.8 is commonly used, but for bright nickel deposits, lower figures (2.4 to 4.8) are more usual. At the higher pH values there is less likelihood of gas evolution at the cathode, which in some circumstances may lead to "pitting" of the deposit. (See p. 297.) On the other hand, in solutions where there is a tendency for iron to accumulate, such as in the plating of steel parts, basic iron compounds form in the solution and fail to redissolve at higher pH values; in such cases it may be necessary to work within a lower range to avoid pitting. The hardness of the

deposit is influenced by the pH of the solution, high pH values tending to favour the production of harder deposits than do the low values.⁽²⁾

The pH may be measured electrometrically (using the quinhydrone or the glass electrode) or colorimetrically. Permanent colour standards can be employed, and special disc comparators are available

for nickel-plating solutions (Fig. 87); the method of use is to fill the two 10 c.c. tubes provided with the plating solution and to add to one of them 0.2 c.c. of the indicator solution (e.g. chlorophenol red, bromo-cresol purple, etc., depending on the pH range of the solution). The dial is then turned until one of the discs, when in position before the tube of solution not containing the indicator, produces a colour match with the other tube when both are viewed by transmitted light. The pH can then be read off from a scale on the instrument. It is to be noted that, as generally determined, the colorimetric pH value is usually some 0.5 pH higher than the true electrometric figure. In plating practice it is necessary to determine the pH value of the bath at frequent intervals and to add sulphuric acid from



Fig. 86.—Wear of nickel anodes
(Left) Depolarised anode
(Right) Electrolytic nickel anode

time to time, since the pH usually tends to rise during working.

ANODES

Under modern plating conditions using hot solutions and air agitation, high purity nickel anodes must be employed to obtain uniform dissolution and to prevent their disintegration. The chief types of anodes used in this country are:

- (a) Chill cast anodes,
- (b) "Depolarised" rolled anodes, and
- (c) Electrolytic nickel anodes.

These types of anodes are all of high purity. The British Standards Institution's specification No. 558 (1934) for nickel anodes has the following requirements:

Nickel (with cobalt) not less than	99.0 per cent
Nickel	98.5 "
Iron	0.75 per cent (max.)
Copper	0.25 " "
Silicon	0.1 " "
Manganese	0.1 " "
Carbon	0.3 " "
Zinc	0.01 " "



Fig. 87. —Disc comparator for determining the pH of nickel-plating solutions.

Courtesy of W. Canning & Co. Ltd.

In the course of dissolution of anodes in nickel baths some minute particles of metallic nickel, oxide, etc., are liberated, and if these reach the cathode they will cause roughness or inclusions in the deposit which will consequently have poor corrosion resistance.

The extent to which such loose nickel particles are liberated in all types of anodes is influenced by the methods adopted in the casting or rolling of them, so that, for example, casting temperatures and rates probably have a marked effect on anode corrosion. The presence of slag inclusions, blow-holes, and similar defects may also

have an adverse effect on satisfactory anode performance.⁽²⁾ A characteristic of nickel anodes is an increasing tendency to passivity with increasing purity, and this is counteracted by the addition of chlorides to the electrolyte. The degree of solubility of the anodes is also faster with anodes of low density than with high-density metal.

In the manufacture of anodes the nickel is melted, preferably in electric furnaces, as rapidly as possible to reduce gas absorption, since molten nickel has an affinity for carbon monoxide and sulphur dioxide. Deoxidation is effected by the addition of small amounts of manganese or magnesium. The latter metal is much to be preferred owing to the fact that the oxide and sulphide of magnesium are soluble in the nickel sulphate electrolyte without detriment.

The metal is cast at temperatures of 1650°C. to 1680°C., the temperature being kept as low as possible. Cooling should be rapid at first to prevent the growth of large crystals, but final cooling to room temperature should be slow in order to eliminate internal stresses as far as possible.

Anode Bags.—Nickel anodes are generally bagged to prevent particles finding their way into the plating solution. The bags are usually made of cotton, twill, or calico, but heavier, closely woven fabrics of the sailcloth types have been favoured of recent years in this country, these being more retentive for fine particles. Anode bags of nylon are also very satisfactory. The fabric must be free from dressing to avoid contamination of the solution by organic matter, and it is a wise precaution to boil anode bags in water before use to avoid the possibility of such contamination. An interesting recent innovation has been the introduction of bags in which the bottom few inches have been impregnated with a synthetic resin to make them impervious. This makes the bags less liable to break and more retentive of the minute particles which accumulate in the bottoms of them.

Anode bags of woven glass fabric have been used on a small scale, these materials having the obvious advantage of not introducing organic material into the solution. They are somewhat expensive, however, and their durability leaves much to be desired. Glass anode bags should also be thoroughly degreased before use to remove lubricants used in the spinning of the glass fibres.

Cast Anodes.—Chill cast nickel anodes are the cheapest type to produce and prove satisfactory in solutions operating at low current density. They can be obtained in the form of flat plates, or, better still, of oval cross-section with cast-in brass hooks. The latter anodes dissolve more uniformly than do the flat plates, which often wear

unduly rapidly at the solution line, so that portions of the anode may break off and fall to the bottom of the tank. Cast anodes are readily soluble, but they tend to disintegrate owing to the heterogeneous nature of their crystal structure. Thus in addition to the formation of oxide slime a certain amount of nickel separates from the anodes in the form of fine crystals. These may enter into the solution despite the use of anode bags, and cause rough nickel deposits. This tendency towards the liberation of nickel crystals is accelerated by certain impurities in the nickel, but is retarded by the presence of carbon and silicon.

The disintegration of cast anodes can be markedly reduced if they are subjected to a suitable rolling operation followed by annealing at a temperature of $800^{\circ}\text{C}.$ to $820^{\circ}\text{C}.$ The casting methods used also influence their properties, and uniform, non-porous castings will naturally tend to dissolve more satisfactorily than anodes of a less dense type.

Carbon-type Anodes.—Anodes having a high carbon content were first introduced in the U.S.A., but are being increasingly used in this country. They are available both in the cast and rolled forms. The carbon content may be as much as 0.4 per cent, but 0.2 to 0.3 per cent is more usual. As the anode corrodes an adherent film of carbon and silica (which is also usually present to the extent of about 0.2 per cent) forms on its surface. This film is highly tenacious and serves to prevent minute nickel particles becoming detached and finding their way into the plating solution. Such anodes can be used without bags where air agitation is not employed, but it is advisable to use them as a safeguard in the event of portions of the anode film breaking away.

The action of the carbon is modified by the presence of the silicon. The carbon slime has no appreciable resistance to the passage of current, and tends to adhere to the anode surface. On the other hand, the silica sludges become heavy and fall away so that by these counter-acting actions a uniform film is maintained. These anodes are most suitable for use in unagitated baths as it is desirable that the detached slimes should fall to the bottom of the tank and remain undisturbed.

Rolled Anodes.—With the advent of solutions operating at higher current densities, rolled anodes have tended to replace the cast type, as the latter tend to disintegrate at higher current densities. The solubility of rolled anodes in a given solution can be controlled by the degree of rolling to which they are subjected in manufacture. The denser the structure the lower is the solubility and the greater the tendency for passivity to occur.

“Depolarised” Anodes. At high current densities and pH values, satisfactory anode corrosion is difficult to obtain even with high chloride contents; for operation under these conditions, the “depolarised” type of anode has, therefore, been developed and gives a uniform rate of corrosion even at very high current densities. “Depolarised” anodes are rolled, and contain a carefully regulated proportion of nickel oxide which prevents the formation of a passive film and aids regular dissolution. The oxide content is of the order of 0.5 per cent, and the amount of sulphur present in the nickel must also be very carefully controlled if uniform anode dissolution is to be obtained. Sulphur is normally present to the extent of about 0.003 per cent; the exact concentration is critical, as excessive amounts may cause the anode to disintegrate owing to the segregation of nickel sulphide at the grain boundaries while an insufficient quantity causes ineffective “depolarisation”. More recently the addition of traces of copper to these anodes to improve corrosion has also been claimed.⁽⁴⁾ The metal is subsequently homogenised by rolling, hammering and forging, whereby the cross-section is reduced by about two-thirds. A disadvantage of these anodes is that as dissolution proceeds, the oxide is liberated as a fine brownish slime which is insoluble in the plating solution.

Electrolytic Nickel Anodes.—Electrolytic nickel is produced in plate form in the electro-refining of the metal, and can be used directly as an anode. The nickel is of very high purity, but has a tendency to become passive and to dissolve irregularly, with the result that towards the end of the life of the anode, a porous nickel residue remains which is substantially insoluble in the solution. This residue may be granular and fall to the bottom of the anode bag, or it may hold together weakly, retaining the anode form. In either event a proportion of wastage results. The tendency is especially marked in high pH solutions, and in solutions having a low chloride content. In the case of bright nickel baths working at pH 4.5 or less, they have been used with some success, however, their high purity being advantageous in such solutions. As supplied, electrolytic nickel plates are about $\frac{1}{4}$ in. thick, and it has been found an improvement to cut these plates into strips which are welded together at the top to form a three-ply or five-ply anode of correspondingly greater thickness; such an anode dissolves more satisfactorily and with less wastage. A low-temperature annealing treatment has also been claimed to improve the dissolution characteristics of electrolytic nickel. The annealing temperature used is of the order of 800 °C. and is claimed to refine the crystal structure of

the nickel. Better dissolution can be obtained, however, by subjecting the anodes to a rolling operation prior to annealing. The lower manufacturing cost of electrolytic nickel anodes, coupled with changes in the operating conditions of plating solutions, will tend to favour their use in the immediate future, although up to the present they have only been used to a relatively limited extent. Electrolytic anodes are particularly suitable for use with high chloride solutions in which other types of anodes tend to dissolve too rapidly.

The appearance of a depolarised anode as compared with an electrolytic anode after a period of use is illustrated in Fig. 86.

PLATING CONDITIONS

In the operation of the Watts type of bath the conditions selected should be such as will favour the maintenance of an adequate concentration of nickel ions in the vicinity of the cathode. If this condition is not obtained "pitted" or "burned" deposits will result. The maintenance of the requisite concentration of nickel ions is achieved by:

- (i) A high nickel content in the solution.
- (ii) Relatively high operating temperatures.
- (iii) Movement of the solution to prevent stratification.

The nickel content should be as high as possible consistent with the economic aspect occasioned by the loss of nickel through drag-out, this being naturally much higher with hollow and recessed articles than with those having relatively plane surfaces. The hardness of the deposit is affected by the plating temperature and a medium must be struck between a tendency for burning to occur if the temperature is too low at a particular current density or for the deposit to be too soft and hence difficult to finish if the temperature is too high.

The normal Watts solution is usually worked within a pH range of 5.6 to 5.8, as has already been stated. Within this range less hydrogen is liberated and there is, therefore, less tendency towards pitting from this cause. On the other hand, a high pH solution may result in the precipitation of basic compounds, as has already been mentioned, which may cause pitting also. Phillips⁽⁵⁾ has advocated the use of a low pH solution operating within the range of 1.5 to 3.0; at such pH values there is much less tendency for soluble materials to remain in suspension, particularly where iron is likely to be present in any quantity. This makes for smoother deposits and less liability towards pitting, and the solution has therefore been employed

fairly widely in the U.S.A., where heavy nickel deposits on large steel articles such as automobile bumpers are required. In this country an intermediate pH value of 3.6 to 3.8 has been found by the author to be preferable for products of this class owing to the considerable reduction in the cathode efficiency of nickel-plating solutions which takes place at pH values of less than 2.3.⁽⁶⁾

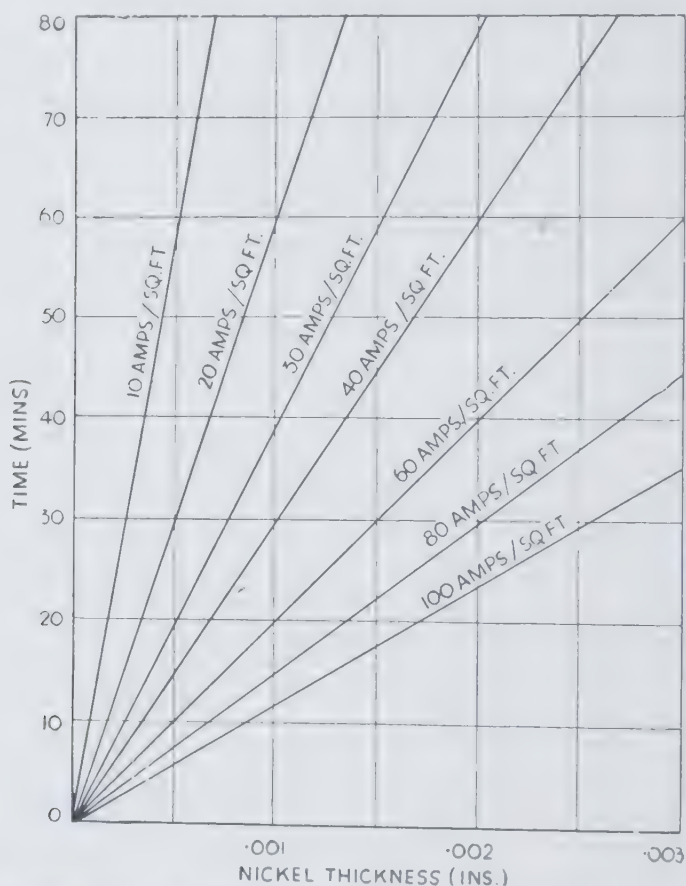


Fig. 88.—Rate of deposition of nickel at various current densities (current efficiency 95 per cent)

Although the low pH solution may permit of the use of higher current densities while maintaining smooth deposits the lower cathode efficiency results in a greater tendency for hydrogen liberation to take place, which may cause pitting of the deposit. The use of "wetting agents" to effect a reduction in the surface tension of the solution is helpful in reducing the tendency for hydrogen bubbles to adhere. (See p. 299.) Current densities of 20 to 40 amps. per sq. ft. are usual with the Watts solution; Fig. 88 shows the rate of deposition

of nickel at various current densities assuming a cathode current efficiency of 95 per cent. The working temperature is around 100° F.

Throwing Power.—The “throwing power” of a nickel solution is usually moderately good, but constant efforts have to be made to improve this characteristic by suitable arrangements of anode-cathode distances and the selection of plating conditions. The protective value of a nickel deposit is greatly dependent on its thickness, so that those factors which make for uniformity in the deposit are to be aimed at. Throwing power and cathode efficiency are interrelated, and it is often found that those solutions having good throwing power operate at high efficiencies.

Generally, increasing current densities result in a decrease in throwing power (except possibly in low pH solutions), but modern production conditions require a high rate of deposition and this tendency must be countered by appropriate measures. Haring points out that good throwing power is favoured by maintaining a high ratio of nickel to hydrogen ions in the cathode film.⁽⁷⁾ In the case of low pH solutions raising the temperature and increasing the nickel content of the solution both lead to improved throwing power, but with solutions of higher pH the effect appears to be less marked. It is desirable to keep foreign metals such as copper, zinc, and iron out of the solution as far as possible; ferric iron, which can exist in low pH solutions in the presence of oxidising agents (where these are employed to reduce “pitting”) is particularly harmful. In general, high pH solutions have better throwing powers than have solutions of low pH.

The Chloride Solution.—Recently the use of a nickel chloride solution in place of nickel sulphate has been advocated by Wesley and Carey,⁽⁸⁾ a typical bath consisting of:

Nickel chloride $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	. . .	30 oz./gall.
Boric acid		3 oz./gall.
pH		1.0 to 5.0
Temperature		120° F. to 150° F.

The pH is adjusted by the addition of hydrochloric acid. It is claimed that the deposit is smooth and easily polished and that the solution can be operated at very high current densities without nodulation or “treeing”. The advantages of the chloride solution are: (a) its high conductivity, which is almost twice that of the sulphate solution, resulting in a considerable saving in power; (b) low pH solutions can be employed without loss of efficiency, which is very desirable where ferrous metals are being plated; (c) excellent anode

corrosion is obtained; (d) the relative absence of pitting; and (e) the fine-grained and ductile nature of the deposit. The chloride nickel solution has not yet been employed on a large scale, partly on account of its corrosive nature (which prevents it from being used in lead-lined tanks). It does, however, appear to have considerable possibilities.

A chloride-acetate solution has also been described⁽⁹⁾ consisting of equal proportions of nickel chloride and acetate operated at a pH of 4.0 to 5.5 and a temperature of 130° F. High current densities of up to 400 amps. per sq. ft. can be employed.

A high chloride strike solution also provides the best means of plating nickel on to stainless steels or steels containing chromium. A typical bath contains:

Nickel chloride	.	.	.	38 to 40 oz./gall.
Boric acid	.	.	.	5 to 8 oz./gall.
Hydrochloric acid	.	.	.	12.5 per cent (by vol.)

The bath is operated at 20 to 40 amps. per sq. ft. at room temperature for 3 to 5 minutes, after which plating is carried out in the usual type of nickel solution.

PLATING OF ZINC-BASE ALLOY DIE-CASTINGS

The use of zinc-base die-castings for the fabrication of many components is one of the most important developments of recent years. The cheapness and rapidity with which such fittings as motor-car horns, handles, radiator grilles, and innumerable components can be produced makes it likely that this technique will become even more popular in the future.

Die-cast parts are employed for mechanical components inside assemblies, and in such cases little or no protection of the metal is needed. A chromate treatment is sometimes advantageous, however, to inhibit the formation of white corrosion products on the metal surface where close fits on moving parts are concerned.

For external use, some finishing is essential, and although organic finishes are employed, chromium-plating is probably the most generally useful and serviceable finish to apply. For plating, die-castings should be free from surface imperfections and have a good dense skin. Normally this skin is only about 0.01 in. thick so that if the surface of the casting is not smooth it may be cut through in polishing, thus exposing the porous interior of the casting. Within limits thin walls are helpful inasmuch as they promote rapid cooling of the casting, and hence a dense, smooth surface. Flat, plain surfaces

should be avoided in design as they emphasise slight surface imperfections. The introduction of curves or fillets is helpful in obtaining a good appearance after plating. Likewise sharp corners should be avoided, whilst deep recesses are undesirable as they make the castings difficult to clean and liable to trap polishing compound, which is not easily removed before plating. The introduction of zinc into the plating solution may also occur by chemical attack on such areas. If such recesses are required to have a bright finish they may also prove difficult to reach with the polishing wheel.

Polishing.—The polishing of zinc-base die-castings is fairly simple and is best carried out with a tripoli composition on calico wheels. The most important point is to avoid excessive pressure as, if the surface skin be penetrated, the porous interior of the casting may be exposed with increased liability for plating difficulties, such as “blistering” and “pitting”, to occur; the durability of the plate will also be poor. More recently abrasive belt polishing has become increasingly popular. After polishing down to about 220 mesh abrasive, the castings are buffed on soft muslin wheels to produce a high surface finish. Small parts may be barrel polished prior to plating.

Cleaning.—In cleaning, prior to plating, it is desirable to degrease the polished castings in trichlorethylene. Vapour degreasing may be adequate in certain cases, but when intricately shaped articles are involved a liquor-vapour plant is essential to facilitate the removal of polishing composition residues. The degreasing operation should be followed by electro-cleaning in a suitable hot alkaline solution to disperse any non-greasy material left after solvent degreasing, together with soap or other films on the metal surface. Cathodic cleaning is most commonly used, since this gives the maximum gas liberation, and hence the greatest dispersing action; sometimes anodic cleaning is employed. In some plants the work may be made cathodic followed by anodic cleaning for a few moments.

The use of anodic cleaning as opposed to cathodic has been advocated by Lewis⁽¹⁰⁾ to reduce blistering on the ground that cathodic cleaning is likely to lead to hydrogen absorption to which some types of blistering may be ascribed. It does seem likely that improved adhesion may be obtained in some instances by the use of anodic alkaline cleaning, particularly in bright nickel-plating solutions.

Strong alkalis attack zinc-base alloys with the formation of discoloured films on the metal surface. Hence only mild alkaline cleaners having a pH not in excess of about 10.2 should be used. A satisfactory cleaner may be made by dissolving 2 to 4 oz. of trisodium phosphate in water and operating the bath at a temperature

of 180° F. to 200° F. The surface tension of such solutions is relatively high, but soaps cannot be successfully used as a cleaner ingredient to reduce this undesirable feature of the cleaning solution since they are decomposed at pH values of less than 10.2. Some of the synthetic wetting agents which are stable in the low pH range are useful in such cleaners, although those excessively prone to foaming are best avoided for practical reasons. A number of proprietary cleaning compositions are available which give excellent results; metasilicate-containing materials are to be viewed with suspicion, however, as they may cause undesirable film formation on the metal surface.

The time of cleaning is important, since blistering and poor adhesion of the plating are sometimes obtained on surfaces which have been over-cleaned as well as on imperfectly cleaned metal. Zinc is a reactive metal and all pre-plating treatments should be as short as possible.

After cleaning, the articles are well washed in running cold water and then dipped momentarily in a dilute solution (about 5 per cent) of sulphuric or hydrochloric acid, until gas evolution first commences. A solution of hydrofluoric acid is favoured in some quarters for this purpose. The acid dip removes the slight oxide film usually left on the metal after polishing and cleaning. The articles are then again washed well and are ready for plating.

Plating.—Two plating systems are in use, viz.: (1) direct nickel, and (2) copper-plating from a cyanide solution, followed by nickel.

(1) *Direct Nickel-plating.*—The usual Watts type of solution cannot be employed for direct plating on zinc since it attacks the metal; it is, therefore, necessary to use a solution which is highly buffered with sodium sulphate; the composition of a typical solution of this kind is as follows:

Nickel sulphate	12 oz./gall.
Sodium sulphate	10 to 15 oz./gall.
Sodium chloride	2 oz./gall.
Boric acid	2 oz./gall.

Operating Conditions—

pH	5.6 to 5.8
Temperature	85° F. to 90° F.
Current density	20 to 30 amps./sq. ft.

The amount of sodium sulphate required depends on the shape of the articles being plated. Where deeply recessed articles are concerned, the relatively poor throwing power of this plating solution

will mean that a longer time will elapse before such recesses are sufficiently covered with nickel to prevent attack by the solution, and thus a greater degree of buffering will be required. The solution should be agitated; current densities of 15 to 35 amps. per sq. ft. are employed, but the solution is unsuited for use at higher current densities.

In spite of the buffer action of the sodium sulphate, zinc tends to dissolve in the solution; this shows itself by the nickel becoming rather bright and hard, whilst further zinc contamination causes dark streaks to occur in the deposit. The throwing power of the solution is also reduced, whilst the deposit becomes brittle. The zinc salts must then be removed by such methods as precipitation with excess nickel carbonate and filtering or by plating out the zinc at very low current densities on to sheet-steel cathodes. This solution produces a reasonably bright deposit although it is likely to be matt at high-current density areas. The sulphate bath cannot be successfully employed for building up nickel deposits greater than about 0.0005 in. thick, as such deposits tend to crack in service. It is, however, possible to deposit greater thicknesses of nickel on the initial nickel deposit from a normal Watts type of bath if the articles are transferred to the second bath immediately after rinsing.

In order to minimise zinc contamination, a high initial "striking" current density is helpful; parts should on no account be put into the plating bath before the current is switched on.

(2) *Copper Undercoats.*—It is becoming increasingly common to pre-copper plate die-castings prior to nickel. The copper is applied from a cyanide solution of the usual type. The free cyanide is controlled at about 1 oz. gallon, and the temperature is about 100°F. Current densities of 15 to 20 amps. per sq. ft. are usually employed.

The Rochelle salt bath is also useful; with this solution, current densities of up to 60 amps. per sq. ft. can be used, smooth deposits being obtained. The thickness of copper required depends on the shape of the articles and to some extent on the pH of the nickel solution employed. With bright nickel solutions operating at pH 4.3 to 4.6, it is unsafe to have less than 0.0003 in. of copper undercoating. It is found that copper deposits are absorbed by zinc quite rapidly, so that an adequate quantity of this metal must be present not only to prevent attack on the zinc by the nickel solution, but to ensure that the copper undercoat is not absorbed during the lifetime of the article. If this occurs, failure of the nickel due to lack of adhesion may subsequently ensue. After coppering, the die-casting is rinsed

successively in hot and then in cold water, dipped in 5 per cent sulphuric acid to neutralise alkali, again rinsed, and transferred to the nickel-plating bath.

The copper undercoat adds little or nothing to the protective value of the plating and the amount of nickel required to meet particular service requirements is not reduced. On the other hand, a copper undercoat permits the normal type of nickel-plating solution to be employed, so that higher rates of deposition can be maintained without risk of "burning", to which the sodium sulphate direct nickel solution is prone.

The increasing use of bright nickel-plating makes a copper undercoat almost essential as no commercially employed bright nickel-plating solution will enable bright plating to be carried out on to zinc directly. It has recently been claimed, however, that the use of selenium enables a bright plating solution to be obtained which can be used for direct plating on to zinc-base alloys.⁽¹¹⁾ A recommended solution given consists of

Nickel sulphate	.	.	.	12.5 to 15 oz./gall.
Sodium sulphate	.	.	.	11 to 16 oz./gall.
Ammonium chloride	.	.	.	2.5 oz./gall.
Boric acid	.	.	.	4 oz./gall.
Selenious acid (SeO ₂)	.	.	.	0.03 to 0.06 oz./gall.

Operating Conditions—

Temperature	.	.	.	110°F.
Current density	.	.	.	24 to 48 amps./sq. ft.
pH	.	.	.	5.8

Chromium-plating is carried out in the usual manner on to the nickel undercoat. No special precautions are needed, even on recessed parts or on internal threads where the nickel deposit is thin or non-existent, as zinc-base alloys are attacked only very slowly by chromium-plating solutions.

Relative Merits.—As to the relative merits of the direct nickel and copper-nickel deposits, a great deal depends on the types of article being plated. Complex-shaped components must be coppered first owing to the poor throwing power of the high sulphate nickel bath. On the other hand copper deposits are more prone to blistering, since copper and zinc tend to diffuse into one another to produce brittle interlayers whilst zinc and nickel do not.

Copper deposits also produce coloured corrosion products which is a disadvantage in service. Nevertheless, with the increasing use of

bright nickel the direct method is becoming less used and copper-plating prior to nickel on die-castings is now almost universal practice.

Fig. 89 shows the front end of a modern British car, which has made extensive use of bright nickel- and chromium-plated zinc-alloy die-castings in its bodywork. The radiator grille is a one-piece casting; the radiator emblem and all handles are likewise nickel- and chromium-plated die-castings.



Fig. 89.—One-piece car radiator grille

Courtesy of Morris Motors Ltd.

Fig. 90 shows an American bicycle headlamp and horn combined; the case and mounting bracket are nickel- and chromium-plated zinc die-castings.

PLATING DEFECTS

Nickel deposits under some conditions are subject to the formation of "pits" or slight depressions in the plated surface which reduce the protective value of the coating and are also unsightly in appearance, particularly when the nickel has been polished. These pits do not always penetrate to the base metal, and the defect is to be distinguished from porosity in the nickel, which will be discussed in greater detail below.

"Pitting" and its Causes.—The causes of pitting have been

the subject of considerable investigation, and some aspects of this defect have already been dealt with. Although, in some instances, apparent pitting may result from a porous condition of the basis metal, true pitting is the result of the attachment of a bubble of hydrogen to the cathode during deposition, which prevents further plating locally. One major cause of pitting is the presence of finely divided basic material in the vicinity of the cathode.⁽¹²⁾ These basic compounds of nickel (and particularly of iron, where this metal is present in the solution to any extent) favour the retention of hydrogen bubbles at the nickel surface. This is emphasised by Hothersall and Hammond,⁽¹³⁾ who point out that local inclusions in the metal and surface imperfections may cause bubbles to form and adhere, and that these irregularities are, therefore, to be regarded as the primary causes of pitting rather than the hydrogen bubbles. Pitting, when it develops, is usually countered by the addition of small amounts of hydrogen peroxide or sodium perborate, which liberates oxygen in the solution more slowly than does the former compound. The hydrogen peroxide has the effect of oxidising basic material and reduces hydrogen bubble formation; it also acts as a depolariser at the cathode and serves to oxidise any organic contaminants which may be responsible for pitting. Excessive quantities of oxidising agent must be avoided, however, especially in low pH solutions containing any appreciable amount of iron, as it lowers the cathode efficiency and the throwing power of the solution, and may produce brittle deposits. An excess is also liable to cause "burning" of the nickel. A typical addition is of the order of 1 pint of peroxide per 1,000 gallons of solution twice daily. The addition of potassium permanganate has been advocated to oxidise organic impurities in plating solutions and to reduce pitting,⁽¹⁴⁾ but this method is little used.

Poor Adhesion.—Lack of adhesion of the deposit is often due to poor cleaning, but other conditions can cause the trouble to occur. If the deposit when removed brings a layer of zinc with it, it is probable that the surface of the casting itself is laminated due to injection into excessively cold dies. If the weak layer is not too deep a longer acid dip prior to copper-plating may serve to remove it, although it is best to correct the fault at the casting stage.

The presence of chromium compounds in the cleaners used will cause poor adhesion and blistering. The chromium enters usually by being carried on plating racks used for direct nickel- and chromium-plating. The addition of sodium hydrosulphite to the cleaner is recommended to eliminate this by reducing the chromic acid, whilst

small amounts of sodium bisulphite added to the bright nickel bath have also been recommended.⁽¹⁵⁾

Use of Wetting Agents.—Wetting agents have also been recommended, and some of these materials are very effective. Very low concentrations, of the order of 0.02 to 0.04 per cent, lower the surface tension of the solution to about half the normal value, thereby reducing the tendency for hydrogen bubbles to adhere to the cathode.



Fig. 90. Bicycle headlamp and horn. The case and mounting bracket are zinc-base alloy die-castings, nickel- and chromium-plated

(Courtesy of National Alloys Ltd.)

Straight chain alkyl naphthalene sulphonates have been found particularly useful, but the amounts employed must be carefully controlled or their presence may result in a substantial reduction in current efficiency and permissible current density.⁽¹⁶⁾ Certain wetting agents must be avoided entirely, as they may lead to the formation of brittle deposits.

A recent investigation into the effects of a number of wetting agents on certain nickel-plating solutions⁽¹⁷⁾ indicated that of the materials tested the most effective from the point of view of stability and the least deleterious in its influence on the deposits was Igepon T ($C_{17}H_{33}.CO.NH.CH_2.SO_3Na$). The smoothest deposits were obtained when the surface tension had been reduced to 38 dynes per

cm. or less. Generally, the effect of wetting agents was to decrease the crystal size of the deposit, this decrease being greater the higher the concentration of the wetting agents. Fig. 91 shows the effect of two of the most satisfactory wetting agents tested, viz. Igepon T and Nekal BX (sodium salt of 1:4 isopropyl naphthalene sulphonic acid) on the surface tension of plating solutions.

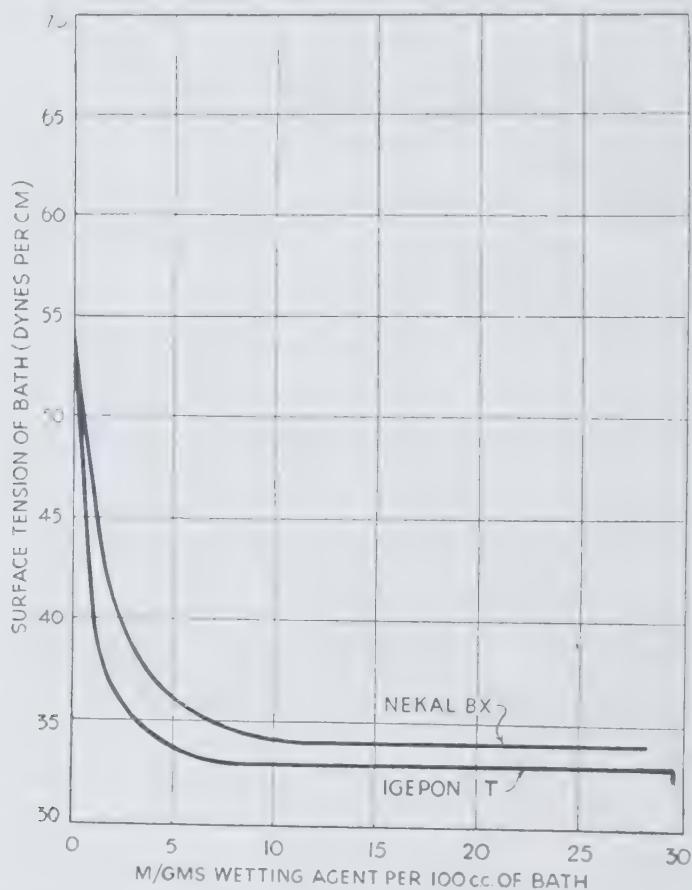


Fig. 91.—Effect of wetting agents on surface tension of nickel-plating solution

Igepon T ($C_{17}H_{33}.CO.NH.CH_2.SO_3Na$); Nekal BX ($C_{10}H_6C_4H_5SO_3Na$)

Porosity in Nickel-plate.—The protective value of commercial nickel coatings is, to a substantial extent, dependent on absence of porosity, particularly as in many instances the nickel coating is cathodic relative to the base metal. A detailed investigation into the causes of porosity in nickel deposits by Hothersall and Hammond⁽¹⁸⁾ led them to the conclusion that the chief factors are: (a) non-conducting or poorly conducting areas in the surface of the basis metal (e.g. inclusions of scale, polishing composition, etc.); (b) the shielding

action of gas bubbles or of particles of solid matter derived from the solution or loosened in etching from the basis metal; and (c) the failure of the deposit to cover the surface of crevices in the basis metal because of poor throwing power or because of exclusion of electrolyte by trapped gas.

It is to be expected from the nature of the growth of an electrodeposit that gaps and pores should occur in its structure by virtue of the fact that many crystal forms are simultaneously taking shape in close proximity to one another so that interference between them

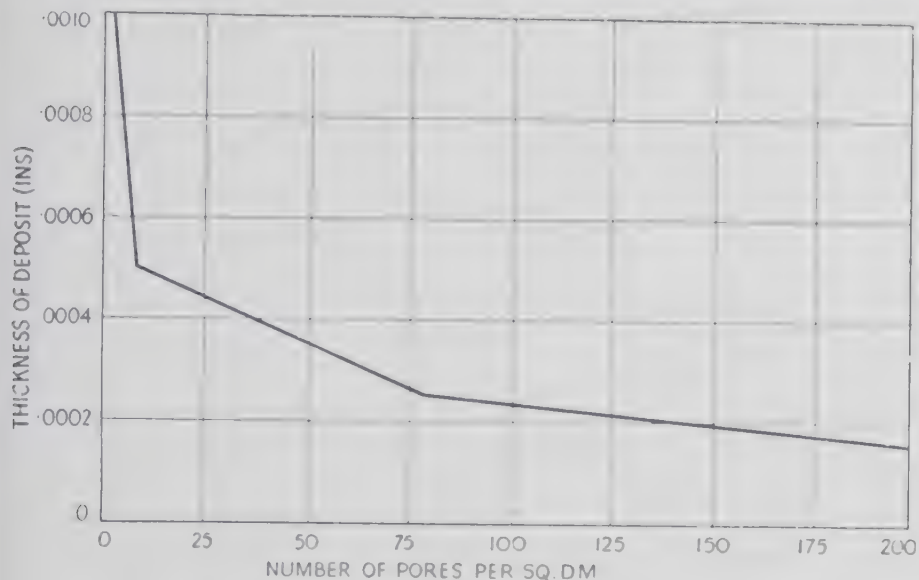


Fig. 92.—Effect of increasing thickness on porosity of nickel coatings

is bound to occur. By virtue of this fact it is almost certain that all deposits are to some degree porous, although this porosity can be greatly increased by the influence of the factors already described.

The influence of pH on porosity was found to be relatively small. It was possible, by careful filtration of the solution and using specially prepared electrolytic iron or finely machined mild steel rod as a base metal, to obtain very thin nickel deposits (less than 0.0001 in. thick) which were non-porous. Under commercial plating conditions, however, some degree of porosity always exists, and for this reason an adequate thickness of deposit must be built up to reduce this to a minimum, since porosity decreases sharply with increasing thickness of plate. When a thickness of about 0.002 in. is reached porosity is negligible, but such deposits are seldom employed in commercial

plating, not only because of cost, but also because heavy deposits are more difficult to finish, being more subject to roughness and nodulation. Fig. 92 shows the effect on porosity of increasing the thickness of a nickel deposit.⁽¹⁹⁾

It should be emphasised, however, that this decrease in porosity may be only apparent because of the increased difficulty of showing porosity with available reagents and methods of test when the length of the pores becomes greater in relation to their width with increasing thickness of deposit.

Rough Deposits.—Roughness is a serious defect in nickel deposits, and is often difficult to eliminate. Roughness troubles increase with increasing thickness of deposit, and apart from the appearance factor such deposits have markedly inferior corrosion resistance. Particles of metal and sludge entering from the anodes are probably the commonest cause of roughness of a type which is characterised by the fact that it appears mainly on the upper surfaces of articles where the particles settle by gravity. Metallic contamination of this kind may also enter from the work or from the plant itself, and must be dealt with by filtration.

Polishing can also result in rough work, especially on steel. If the final polishing operation is carried out with a dry wheel small particles of steel can adhere to the work by magnetic attraction and act as centres for the growth of nodules.

Impurities in Nickel Solutions.—The effects of impurities in nickel-plating solutions are considerable. Nickel solutions are probably more susceptible to impurities than almost any other types of solution in commercial use. The chief sources of contamination are: (a) anode sludges; (b) metallic impurities, such as copper, iron, and lead, introduced from metals in contact with the solution or articles being plated; (c) dust and grease from the atmosphere, from compressors, or from materials entering the solution unintentionally on articles being plated; (d) insoluble constituents, due to the use of hard water for making up the solution or present in plating chemicals; (e) organic contamination, resulting from the breakdown of organic addition agents.

Anode sludges can be largely prevented from entering the solution by the use of suitable anode bags, but a certain proportion of fine sludge seeps through the material of which the bags are made, or accidental tearing of the bags may cause trouble. All forms of insoluble materials of this kind tend to settle on the cathodes, particularly on horizontal or inclined surfaces, despite agitation of the solution, resulting in rough deposits.

Iron is a common constituent of nickel solutions, particularly where ferrous metals are being plated. Normally, the presence of a little iron is not deleterious, but in high pH solutions basic ferric hydroxide particles may cause roughness. Copper and zinc adversely affect throwing power and result in dark deposits when they are present in excessive amounts. They are particularly undesirable in bright nickel solutions. As little as 0.03 gm. l. of zinc shows itself in a brightening and embrittlement of nickel deposits, especially at low current densities. More than 0.3 gm. l. of zinc in a warm nickel solution brightens the deposit; cracking and poor corrosion resistance develop and reach serious proportions at about 0.6 gm. l. Streaky deposits appear at zinc contents below this figure, but the streakiness is less evident at higher bath temperatures.

Chemical methods are available for the purification of nickel solutions which have become contaminated. Precipitation of iron salts and zinc can be effected by adding nickel carbonate till a pH of about 6.2 is reached, followed by filtration of the precipitated salts. This method is based on the fact that ferric iron starts to precipitate at a pH of 4.7 and ferrous iron at 5.5. Both zinc and copper hydroxides are precipitated at pH 5.8 to 6.0, and trivalent chromium at a pH of 6.0 to 6.2. A pH of 6.6 should not be exceeded, since nickel hydroxide commences to precipitate at this stage. Copper in a nickel-plating solution progressively reduces the salt spray resistance of the deposit; 10 mg. l. of copper in a Watts' solution in one series of experiments reduced the resistance by 30 per cent, whilst at 40 mg. l. of copper the corrosion resistance of a deposit 0.001 in. thick was halved.⁽²⁰⁾

Filtration.—In current practice, where high-speed nickel-plating is being carried out, filtration of the solution is almost essential, and this may be carried out either continuously or intermittently. The subject of filtration in relation to plating solutions has already been discussed in detail (p. 242), and is referred to again here because of the supreme importance of filtration in nickel-plating practice. Diatomaceous earth is commonly employed in filters to remove suspended matter, but where contamination with organic material has occurred, the use of activated carbon is recommended. This will remove emulsified oil, organic degradation products of addition agents, sizing which may have been introduced on anode bags, etc. The usual procedure is to add about 0.5 to 1 per cent of activated carbon by weight to the bath, heat to about 140° F., agitate for a period, and then filter off the carbon when the contaminant will be removed, together with the carbon.

The sensitivity of nickel-plating solutions to the presence of foreign metals and the difficulty of finding metals to withstand the solution, especially in the presence of possible stray electric currents, has led to a search for suitable non-metallic materials, from which pumps, filters, etc., can be constructed; rubber, glass, stoneware, and special reinforced plastic materials have all been employed to

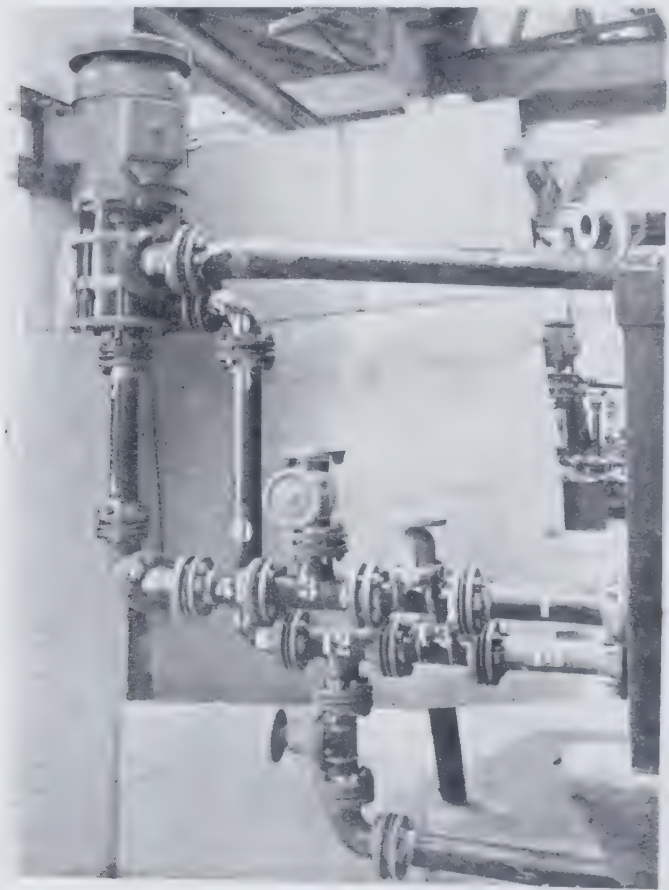
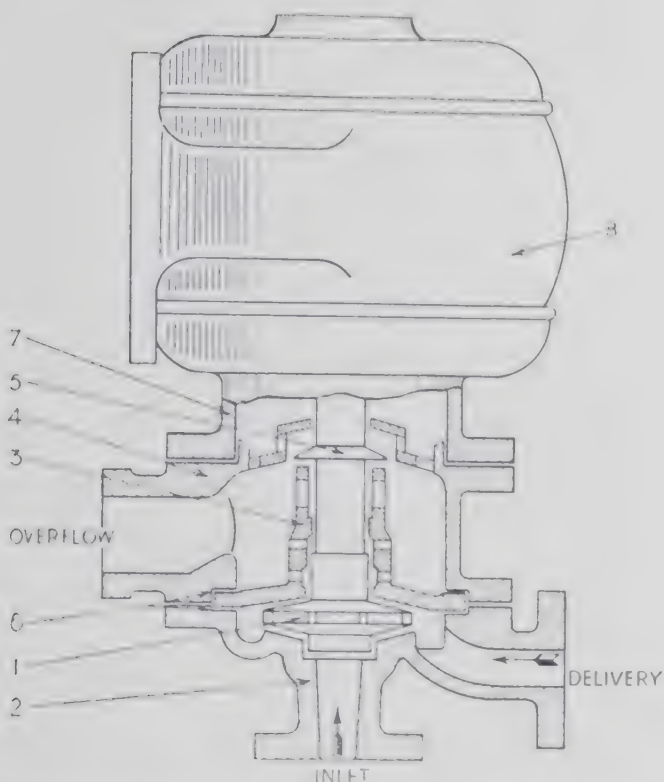


Fig. 93.—Glandless pump constructed of non-metallic reinforced plastic material. Pipes and valves, etc., are of similar fabrication

[Courtesy of Kestner Evaporator and Engineering Co. Ltd.]

some extent. Reinforced plastics of suitable composition present many advantages, and recent developments in plastic technology will lead to an increased use of these materials. Fig. 93 shows a glandless pump, made entirely of a non-metallic plastic; the valves and pipe connections and unions are also of similar material. The construction of the pump can be seen from Fig. 94.



Ref.	Description	Ref.	Description
1	Rotor	5	Thrower
2	Lower rotor casing	6	Joints
3	Upper rotor casing	7	Motor stool
4	Upper body	8	Motor

Fig. 94.—Construction of plastic pump illustrated in Fig. 93

[Courtesy of Kestner Evaporator and Engineering Co. Ltd

BRIGHT NICKEL-PLATING

Bright nickel-plating is now a process of major importance, and it has been stated that in the U.S.A. more nickel anodes are consumed in bright nickel baths than in all other nickel solutions combined.⁽²¹⁾ The advantages of being able to plate nickel bright without the need for polishing are many, the chief being:

- (1) The elimination of the cost of nickel finishing, which is considerable.
- (2) Avoidance of the waste of nickel in the buffing operation, during which as much as 30 per cent of the metal deposit

may be removed, with a corresponding loss in the protective value of the deposit.

- (3) Nickel-plated articles can be directly chromium-plated without the need for drying, unracking, re-wiring, etc.

Attempts to produce a lustrous finish on nickel-plate by the addition of various materials to the plating solution have been described in early publications; cadmium salts have long been known to act as brighteners in nickel solutions, as have colloidal materials, such as glue and gelatine. These additions did not find extended use, however, owing to their uncertain effects and the difficulty of controlling the plating solutions containing them.

One of the first processes to be commercially applied was that of Schlöter,⁽²²⁾ who developed a solution in which aryl sulphonic acids (preferably polysulphonic acids) were added to a Watts type of solution as brighteners. A typical bath consists of:

Nickel sulphate	.	.	.	175 gm./l.
Nickel chloride	.	.	.	85 gm./l.
Boric acid	.	.	.	20 gm./l.
Sodium naphthalene trisulphonate	.	.	.	35 gm./l.

Operating Conditions—

pH	.	.	.	.	2.5 to 4.5
Temperature	.	.	.	.	120°F. to 130°F.

Since then a large number of solutions have been developed and many have been operated commercially on a very large scale. All the bright nickel baths are proprietary, and are based fundamentally on the Watts nickel sulphate solution with various additions. A list of some of the more important patents is given in Table XXXIII, with an approximate indication of the nature of the brighteners employed. The bright nickel patent situation has been surveyed by Young.⁽²³⁾

Types of Brighteners.—An examination of the compositions of bright nickel-plating solutions shows that the brightening addition usually consists of two or more constituents. It can be said, broadly speaking, that the classes of materials employed fall into two groups. These are: (a) materials which act as very effective brighteners, but which must be used in carefully regulated quantity. Within this group are substances such as cadmium and zinc salts, aldehydes, selenium and tellurium, glue, gelatine, and dextrin. The range of concentrations within which these brighteners can be employed is

TABLE XXXIII
PRINCIPAL BRIGHT NICKEL-PLATING SOLUTIONS

Solution		Brighteners used
Schlötter	U.S.P. 1,972,693 (1934)	Nickel benzene disulphonate; naphthalene trisulphonate
Weisberg and Stoddard	U.S.P. 2,026,718 (1936)	Cobalt sulphate, sodium formate and formaldehyde
Harshaw	U.S.P. 2,029,386 (1936)	Sulphonated oleo-resins
	U.S.P. 2,029,387 (1936)	Sulphonated terpenes
Hinrichsen	B.P. 461,126 (1937)	Cobalt sulphate and sodium formate
Hull	U.S.P. 2,085,754 (1937)	Organic ketones
Harshaw	U.S.P. 2,125,229 (1938)	Selenious acid and naphthalene disulphonate
McGean	U.S.P. 2,112,818 (1938)	Zinc or cadmium, and naphthalene sulphonic acids
	U.S.P. 2,114,006 (1938)	Zinc or cadmium, and sulphonated amino-toluenes
Harshaw	U.S.P. 2,198,267; 2,238,861; 2,290,342; 2,291,590; 2,294,311; 2,315,802; 2,326,999; (1940-43)	Naphthalene sulphonates, amino-polyaryl methanes (e.g. fuchsin) and sodium lauryl sulphate. Sulphonamides and sulphonimides.
Udylite	B.P. 529,825 (1940)	Ketones and aldehydes, e.g. formaldehyde and chloral hydrate
Udylite	U.S.P. 2,191,813 2,240,801; 2,321,182; (1940-46) B.P. 525,847 (1940) 529,825 (1941)	Zinc or cadmium and sulphonamides (e.g. <i>p</i> -toluene sulphonamide); halogenated aldehydes, toluene sulphonic acids.

so narrow that they cannot be satisfactorily used under commercial conditions. Excess quantities soon reduce the cathode efficiency, particularly at low current density areas, so that there may be no deposit at all in recessed parts of articles being plated. Moreover, very slight changes in the operating range of the bath or in brightener concentration may lead to dark and brittle deposits. For these reasons there are added (*b*) substances which, although they may or may not be brighteners in themselves, have as their chief characteristic the ability to make the solution tolerant of a much higher concentration

of the primary brighteners already mentioned. Amongst the substances of this group so far developed are cobalt salts, naphthalene sulphonates, polysulphonic acids, and aryl sulphonamides.

A combination of materials from these two groups is selected and used in appropriate concentrations to give a solution which will have the maximum plating range as regards temperature and current density, and will be reasonably insensitive to the presence of impurities in the solution. The addition agents should obviously have high solubility and should not precipitate out of the solution. Moreover, they should not have an adverse effect on the protective value of the nickel deposit; this is very important.

Anti-pitting Agents.—Practically all the bright nickel solutions using organic addition agents are subject to pitting unless a small concentration of a suitable wetting agent is included. In such solutions hydrogen peroxide cannot be added as an anti-pitting agent owing to the likelihood that it will oxidise the organic brighteners present. Amongst the chief wetting agents employed in commercial solutions are sulphonated alcohols and alkyl substituted aryl sulphonates. The presence of these wetting agents may cause difficulty by emulsifying oils or other contaminants, necessitating filtration or treatment with activated carbon, as has already been described. There is no chemical method for controlling the wetting agents in solution since they are only present in very small concentration; control is, therefore, best carried out by surface tension measurements, using a stalagmometer or similar apparatus.⁽²⁴⁾

Organic Solutions.—The solutions with organic addition agents are almost all proprietary and give a high degree of brightness. As compared with the cobalt-formate type of bath these solutions are a little more difficult to control, and there is a tendency for the additives to break down so that periodic treatment with activated carbon to remove degradation products may be needed. On the other hand, they are lower in running costs as the use of expensive cobalt salts is eliminated. The nickel deposit tends to be rather yellower than the cobalt-nickel alloy deposit, and this effect is often visible even after chromium-plating. Where large-scale plating is being carried out the economic advantages of the organic baths are so great that they are well worth installing, despite the fact that there may be two or more organic additives to control and the fact that the deposit may be rather more highly stressed. The baths operate over a very wide range of current densities, and show little tendency to "burning" even at very high current densities. Control of the addition agents is usually carried out by empirical methods of test.

For the plating of zinc die-castings the sulphonamide type of solution based on nickel sulphate tends to be somewhat unsuitable because of its sensitivity to zinc contamination. One method of overcoming this disadvantage is to use a high chloride bath, as in the Udylite bath for zinc-base alloys. This solution contains 32 oz. of nickel chloride, 14.5 oz. of nickel sulphate and 6 oz. of boric acid per gallon, together with the two necessary organic brighteners and a wetting agent. The bath is operated at 40 to 80 amps. per sq. ft. at a temperature of 135° F. to 145° F. The pH range is from 2.5 to 4.8. This solution has a high zinc tolerance, but lead must be avoided. Owing to the corrosive nature of high chloride solution, lead cannot be used for pipes or other equipment, which is best made of rubber-lined steel. Cathode agitation is recommended, whilst the anodes should be of cast, electrolytic, or rolled nickel. Depassive anodes tend to dissolve too rapidly in high chloride solutions and may cause rough deposits to be produced.

The Cobalt-Formate Solution.—Bright nickel-plating solutions based on additions of cobalt sulphate and sodium formate are of exceptional importance, since these solutions have received a good deal of attention in the literature, and, moreover, practically all bright nickel-plating carried out on any scale in this country has been from solutions of this type. These solutions have an outstanding advantage in that unlike those solutions already mentioned, using complex organic addition agents, all the constituents are controllable by chemical analysis, and their concentration is not critical. There is also no evidence that any of them are liable to break down or polymerise during operation of the bath.

Two nickel-cobalt-formate processes have been used on a large scale:

(1) **The Weisberg and Stoddard Process.**⁽²⁵⁾—This solution utilises cobalt sulphate, nickel formate, and formaldehyde as the brighteners, the composition of a typical solution being:

Nickel sulphate	.	.	.	240 gm./l.
Nickel chloride	.	.	.	30 gm./l.
Nickel formate	.	.	.	45 gm./l.
Boric acid	.	.	.	30 gm./l.
Cobalt sulphate	.	.	.	2.6 gm./l.
Ammonium sulphate	.	.	.	0.8 gm./l.
Formaldehyde	.	.	.	2.5 gm./l.

Sodium formate can be used in place of nickel formate although it tends to increase the hardness of the deposit.

The pH is maintained at 3.5 to 4.5 and the working temperature is about 140° F. Agitation of the solution or rapid cathode bar movement is essential, and under these conditions plating current densities of 40 to 60 amps. per sq. ft., or even higher, are readily realised. Sodium formate serves to buffer the solution within the operating pH range and also contributes to the brightness of the deposit. In the absence of cobalt sulphate the deposit is smooth, fine grained, and easily polished even at high current densities, but is not fully bright. The addition of cobalt sulphate to the solution results in a plate of mirror brightness, which is rather whiter in colour than a pure nickel coating. The cobalt content of this bath is considerably less than that used when the process was in its early stages of development, which makes for lower operating costs. The deposit contains 1 per cent of cobalt, but by increasing the cobalt to 5 per cent, or, for special applications to 18 per cent, whiter and rather more protective deposits are obtained. Nickel-cobalt anodes are necessary with the low cobalt solutions. Boric acid appears to increase the limiting current density at which burning of the deposit manifests itself. Ammonium sulphate in small quantity acts as a brightener, but owing to the well-known hardening influence of ammonium salts, excessive quantities must be avoided or the ductility of the deposit will be impaired. The quantity used should not exceed 1 gm. per litre. The formaldehyde is said to act as a depolariser and anti-pitting agent.

(2) **Hinrichsen Process.**⁽²⁶⁾—This solution is substantially the same as that of Weisberg and Stoddard, except that no formaldehyde or ammonium sulphate additions are made. This simplifies the maintenance of the solution and makes working conditions better, since formaldehyde vapour tends to be rather irritating to the throat and eyes. Moreover, the ready volatility of this constituent makes frequent additions necessary in order to maintain the recommended concentration. Generally speaking, the Hinrichsen solution gives results which are very similar to those obtained from the Weisberg and Stoddard bath. In practice in this country, however, it is customary to work with a higher cobalt content than is present in the newest Weisberg and Stoddard bath, up to 15 gm. l. of cobalt sulphate being employed. Such a bath is more tolerant of impurities.

Cobalt.—Since cobalt is co-deposited with the nickel, the cobalt content of the solution must be maintained. This can be done by using nickel-cobalt alloy anodes, but in this country it is the practice, however, to employ nickel anodes and to add cobalt sulphate to the solution periodically in accordance with the analysis. The cobalt

content of the deposit decreases with increasing current density. Fig. 95 shows the cobalt content of the deposited alloy at various current densities, as given by Weisberg.⁽²⁷⁾ Owing to the relatively high cost of cobalt as compared with nickel, it is therefore more economical to plate at high current densities than at low.

The brightness of the deposit is maintained through considerable thickness of metal, and, in fact, increases as the deposit thickness increases. Pitting is not very prevalent in this type of solution, but if it should be noticeable hydrogen peroxide can be added in the usual amounts.

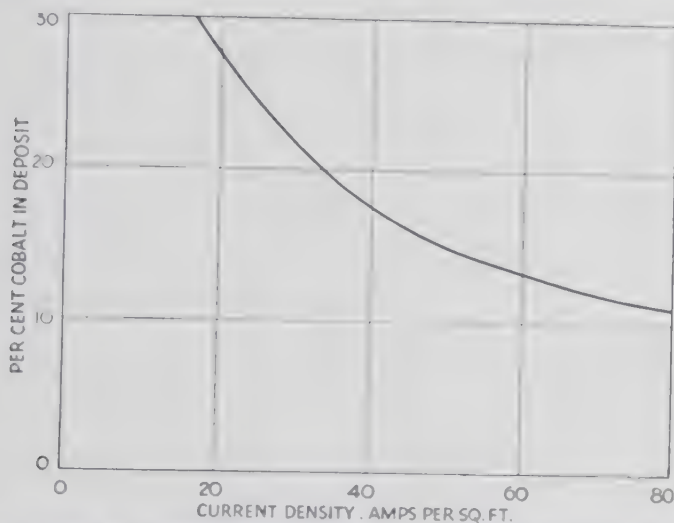


Fig. 95.—Effect of plating current density on cobalt content of deposit from Weisberg and Stoddard bright nickel-plating solution

Effects of Impurities.—All bright nickel solutions are susceptible to the effects of impurities, roughness resulting from the presence of suspended matter, while dissolved substances may also affect the character and brightness of the deposit. For this reason careful attention must be given to the materials of which the tanks are made, and periodic filtration and purification are required, as has already been indicated.

Some solutions are more sensitive to impurities than others. Thus, the Schlötter solution tends to produce dark or brittle deposits, particularly in recessed areas, if the zinc or copper contents exceed 0.5 and 0.1 gm. per litre respectively.

Electrolysis at very low current densities serves to remove lead, copper, iron, and zinc from the cobalt-formate solutions.

Probably the best method of purification is by the use of an auxiliary tank through which the solution circulates and which is

fitted with nickel anodes and corrugated steel or woven wire cathodes. The anode-cathode distance should be kept small and a low current density of about 2 to 5 amps. per sq. ft. maintained constantly through this bath whilst the plant is working. In this way it is found that 0.02 to 0.05 ampere-hour per gallon of plating solution per hour of operation is sufficient to keep the average bath free from contamination. The rate of circulation through the purification tank should be sufficient to deal with about one-third of the contents of the bath every hour. Continuous electrolytic purification does not in all cases replace periodic cleaning of the solutions, although intervals between complete filtrations can be considerably lengthened. The efficiency of removal of zinc and iron are increased by rapid agitation.⁽²⁸⁾ It has also been claimed that chromium can be removed from nickel solutions by low-current density electrolysis if it is first reduced to the trivalent state.

Tests indicate that the rate of removal of the zinc is not greatly influenced by variations in pH or temperature of the solution. The actual rate of removal of the zinc is of the order of 0.012 gm. l. per amp. hour of current. Where there is a high degree of contamination and rapid removal of the zinc is necessary, precipitation with basic nickel carbonate is resorted to. The pH of the solution is raised to about 6.5 by the addition of the nickel carbonate in the form of a slurry at a temperature of about 70°C.; the bath is allowed to stand for about one hour and the precipitate filtered off. Some nickel and cobalt are lost also by this method.

The nickel-cobalt bright nickel bath is perhaps more susceptible than the organic solutions to contamination but with all bright solutions suitable precautions must be taken to prevent contamination. The solution must be continuously filtered and rubber-lined tanks should be used, lead linings being quite unsuitable. The best method of heating is by means of an external heat interchanger; the interchanger can be connected between the filter and the return line to the plating tank with means for by-passing the filter during the initial heating up of the bath. It is, however, preferable to have a separate pump for the heating unit. The interchanger can be made of high-silicon iron or graphite; in the U.S.A. Pyrex glass heat interchangers have been employed, although this material has a somewhat lower heat transfer coefficient.

Agitation of the bath is usually by means of perforated air pipes on the bottom of the tank, the pipes being constructed of ebonite, Keesbush, or a similar non-metallic material.

It is desirable wherever possible to arrange for direct transfer from

the bright nickel to the chromium tank without unranking, as it is in this way that the greatest economies are obtained, particularly in automatic plants. Direct transfer is effected without serious trouble in many large British plants; in the United States, however, it is often the practice to re-rack work before chromium-plating, in which case a further cleaning cycle is introduced prior to the latter operation.

In arranging for the transfer of racked work from the bright nickel to the chromium-plating bath directly, care must be taken to ensure that the racks do not trap solution. If this occurs, chromic acid may eventually be introduced into the nickel solution where it will reduce the efficiency of deposition very considerably, or if sufficient enters the bath, its effect may be to render the bath unusable. Rack insulation kept in good condition minimises this danger, but it is a useful precaution to dip racks in an oxalic acid or sodium hydrosulphite solution after passage through the chromium tanks in order to reduce any chromic acid that may have been retained in them.

According to Macnaughtan and Hammond⁽²⁹⁾ the presence of 0.025 to 0.20 gm. l. of chromic acid in a nickel solution caused a decrease in cathode efficiency, and at 0.220 gm. l. deposition ceased whilst the evolution of hydrogen increased; 0.01 to 0.025 gm. l. resulted in an increase in the stress of the deposit with some exfoliation. Chromium sulphate when added to give a chromium concentration of 0.149 gm. l. caused the cathode efficiency to fall to 81 per cent. The deposit increased in brightness with a tendency to peel; the anode efficiency was not affected. Hothersall and Hammond⁽³⁰⁾ found that chromic acid increased the evolution of hydrogen at the cathode and did not stop pitting. The lower the pH of the nickel bath, the less hydrogen was evolved and the higher the stress in the deposit.

Chromium contamination is difficult to remove. Electrolysis at a pH of 2, using very high current densities in conjunction with lead anodes, enables the chromium to be removed as lead chromate.⁽³¹⁾ Chromium can also be removed by precipitation of the chromium as lead chromate by the addition of lead carbonate,⁽³²⁾ but the introduction of lead salts into the solution is best avoided.

Control by Plating Cells.—A useful method of controlling impurities in bright plating solutions is by means of specially designed test plating cells. One of the best-known types is the Hull cell (Fig. 97). The function of this cell is to provide by geometric configuration a cathode deposit on a flat surface that records reproducibly the character of the deposit produced at all current densities within the

operating range. The cathode plate is inclined at an angle to the anode so that by measuring the distance of the bright plating range from the end of the plate the limiting current density can be derived from a curve. Polished cathodes about $2\frac{1}{2}$ in. by 4 in. are satisfactory and the current should be about 3 amps. at 12 volts. Chromium requires about 5 amps. A certain amount of experience is required in interpreting the results, but a good deal can be learnt about the causes of defects occurring in a bright nickel solution as a result of a Hull cell test.

Mechanism of the Brightening Effect.—The causes of the brightening action of addition agents have been the subject of a good

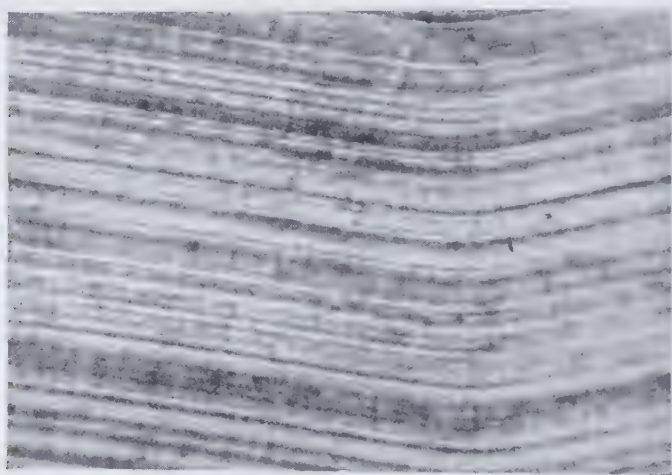


Fig. 96.—Etched section of deposit from Weisberg and Stoddard bright nickel-plating solution

deal of speculation. Schlötter⁽³³⁾ ascribes the brightening effect of aryl sulphonic acids to the reduction in the grain size of the nickel deposit by the specific influence of the anion used; the grain size of bright nickel deposits is of the order of 0.000004 in. or less.

A detailed examination of the structure of bright nickel deposits produced by three of the best-known commercial processes has been carried out by Hothersall and Gardam;⁽³⁴⁾ these authors showed that all the deposits were abnormally hard and fine-grained. The micro-structures showed evidence of periodicity in deposition, resulting in a laminar structure. Fig. 96 shows the structure of the deposit obtained from a Weisberg and Stoddard bath; the parallel lines are depressions caused by preferential etching. This rhythmic structure appears to be characteristic of deposits from bright plating solutions of all kinds.⁽³⁵⁾ Moreover, carbon

was present in all the samples, indicating that the organic addition agent was occluded in the deposits; the carbon content of the three deposits examined were 0.05 per cent, 0.083 per cent, and 0.2 per cent respectively.

Henricks⁽³⁶⁾ is of the opinion that bright plating in the presence of organic addition agents is brought about by a mixture of organic bases and inorganic colloids in the cathode film, which transforms normal deposition into a periodic phenomenon, reduces the grain size of the depositing metal, and restrains perpendicular grain growth

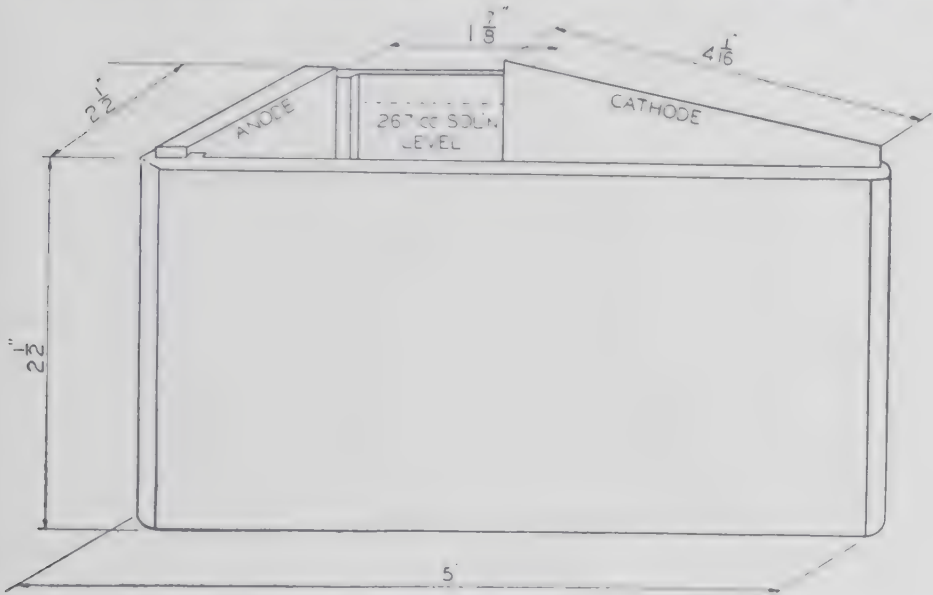


Fig. 97.—Hull cell

by their adsorption. The banded structure in the case of bright nickel deposits based on sulphonic acids or similar compounds would then be a result of a reduction cycle, whereby these compounds are reduced to mercaptans at points of high current density. The polar sulphur group is then adsorbed to form an insulating inhibitor film. The non-polar portion of the molecule is next electrolytically decomposed to sulphur, which is left in the deposit, probably as nickel sulphide; the preferential attack on this constituent by the etching acid gives the characteristic banded structure when a sectioned bright nickel deposit is etched. The presence of sulphur in such bright nickel deposits to the extent of 0.02 to 0.06 per cent has been reported.

The laminar structure of bright nickel deposits may be a source of weakness, and peeling of nickel-plating as a result of adhesion failure

of the layer of organic ions or micelles which have been deposited between successive layers of nickel is not uncommon. Planes of weakness can also occur as a result of the presence of impurities in the solution which deposit at a lower voltage than the primary metal. For example, copper, if present in a nickel solution, can be preferentially deposited as a result of momentary fluctuations in voltage resulting from poor or interrupted contacts or other variations in the conditions of deposition, causing planes of weakness to be set up in the deposit.

Recent work has shown that there is no overall relation between preferred orientation in a bright nickel deposit and the brightness of the plate.⁽³⁷⁾ This applies to a very large number of brightening agents which were tested. X-ray diffraction patterns have shown that it is possible to have as high a degree of fibering in a very dull deposit as in a bright one, or to have any degree of fibering in both bright and dull deposits.

Gardam, investigating the smoothing action which takes place in right nickel-plating on serrated cathodes, found that there are two distinct smoothing actions. One type, shown particularly by solutions containing zinc or cadmium, was in the form of a large-scale smoothing action which filled in the serrations, whilst the other gave a sub-microscopic smoothing effect resulting in brightness. Most commonly used brighteners possessed only the aptitude for producing the latter effect. This is confirmed by the fact that these organic brighteners, such as sulphonates, brightened rapidly in the early stages of deposition and then more slowly, whilst solutions containing zinc or cadmium exhibited progressive brightening as the thickness of the deposit increased, although the final result may not have been fully lustrous. According to Gardam, the presence of sulphur and carbon in bright deposits from sulphonate-containing solutions is incidental to, and not the cause of, brightening. This is because the sulphonates tend to be occluded on the crests of the deposit and not in the hollows and thereby result in an increase in the deposition potential at these points.⁽³⁸⁾

TESTING AND SPECIFICATIONS

In the testing of nickel deposits the thickness of the metal is most important, and can be determined by means of the method of sectioning and polishing a plated sample article. A much more rapid method which is sufficiently accurate for control purposes is the B.N.F. Jet Test,⁽³⁹⁾ in which a solution of ferric chloride and copper sulphate is directed on to the deposit. The time of penetration of the

coating at a particular temperature is proportional to the thickness according to a definite scale.

The adhesion can be determined by rubbing hard with the back of a penknife or similar instrument. If adhesion is poor, blistering of the deposit will show itself. Ollard⁽⁴⁰⁾ has described a method whereby an accurate measure of the adhesion in terms of the pull required to separate the coating from the base metal can be made. A thick deposit of about 1/10 in. must be applied, after which the specimen is machined, as shown in Fig. 98. The hatched area shows the deposit, which is built up on the end of a cylinder of the

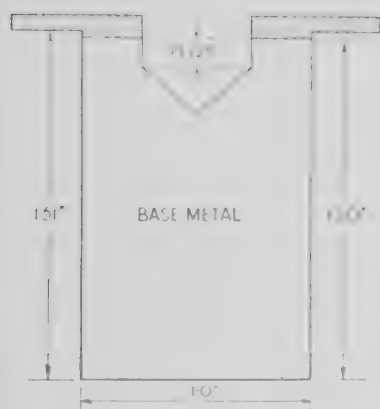


Fig. 98. Specimen for testing adhesion of nickel deposits.

required base metal. Pressure is then applied to the hollowed part of the specimen by means of a tensile-test machine while it is held in a suitable die. The force required to separate the ring of nickel deposit can then be expressed in tons per sq. in. With anodic etching in sulphuric acid on a mild steel base adhesion values of 16,000 to 18,000 lb. per sq. in. are obtainable.

Another adhesion test in which a succession of blows by a vibrating hammer is employed has been introduced more recently.⁽⁴¹⁾

The corrosion resistance of the deposit can be tested by the salt-spray method or by the well-known ferroxyl test. Immersion in hot water has also been employed to determine porosity.

The American Society for Testing Materials in conjunction with the American Electroplaters' Society has issued specifications for nickel deposits on steel, zinc-base, and copper alloys. These are summarised in Table XXXIV.⁽⁴²⁾

The most recent development in this country has been the issue of specifications by the British Standards Institution (B.S.S. 1224: 1945). The requirements as regards thickness of nickel are shown in Table XXXV.

The points at which minimum thickness tests may be carried out are defined as those which can be touched by a sphere of 1 in. diameter.

The author has dealt with the special requirements of plated coatings for the automobile industry elsewhere.⁽⁴³⁾

Nickel-plating processes are being continually developed, the chief

TABLE XXXIV
SUMMARY OF A.S.T.M./A.E.S. SPECIFICATIONS

Basis metal	Service		
	Severe	General	Mild
<i>Steel—</i>			
Copper + nickel, min.	0.00125 in.	0.00075 in.	0.0004 in.
Final nickel, min.	0.0006 in.	0.0004 in.	0.0002 in.
Chromium, if required, min.	0.00001 in.	0.00001 in.	0.00001 in.
20 per cent salt spray, continuous 95° F.	72 hours	48 hours	16 hours
<i>Zinc-base alloys—</i>			
Copper + nickel, min.	0.00125 in.	0.00075 in.	0.0005* in.
Copper, min.	0.0004 in.	0.0003 in.	0.0002 in.
Final nickel, min.	0.0005 in.	0.0003 in.	0.0003 in.
Chromium, if required, min.	0.00001 in.	0.00001 in.	0.00001 in.
Salt spray, as above	48 hours	32 hours	16 hours
<i>Copper alloys—</i>			
Nickel, min.	0.0005 in.	0.0003 in.	0.0001 in.
Chromium, if required, min.	0.00001 in.	0.00001 in.	0.00001 in.

* Total of 0.0003 in. nickel if used without undercoating.

Note.—For very severe conditions on steel, Type DS is specified. This requires a copper and nickel deposit of 0.0020 in. of which the final nickel must not be less than 0.0010 in.

TABLE XXXV
BRITISH STANDARD SPECIFICATIONS FOR NICKEL DEPOSITS

Description	Minimum thickness deposited on significant surfaces	
	Mild and low alloy steels	Brass and copper
Severe outdoor conditions or extra hard wear	0.0008 in.	0.0006 in.
Normal outdoor conditions or hard indoor wear	0.0005 in.	0.0003 in.
Ordinary indoor conditions	0.0003 in.	0.0002 in.

directions of improvement being concerned with better and more readily controlled bright solutions and baths with increased throwing power and capable of being operated at higher current densities.

Concurrently, rapid progress is being made on the engineering side in connection with the fulfilment of such needs as better mechanical equipment, filtration plant, and tank linings.

Nickel-plating is also applied in considerable thicknesses for the building up of worn parts or for wear resistance, but this is a special type of work, and does not come within the scope of the present survey.

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CHROMIUM-PLATING

Chromium-plating is a relatively new process, and its general application in industry does not date back more than about fifteen years. Electro-deposited chromium is a very hard metal, having a characteristic bluish cast with very high resistance to tarnish. In current metal-finishing practice it is usually applied as an exceedingly thin deposit (about 0.00001 in. to 0.00005 in. thick) to give non-tarnishing properties to an underlying electro-deposit (usually nickel), which serves as the main protection for the base metal to which it is applied.

Very much heavier deposits are applied in the engineering industry for imparting wear resistance and low frictional properties to rubbing surfaces, such as bearings, moulding tools, inspection gauges, cylinder bores, etc. The latter group of uses is becoming of increasing importance and has an extensive literature of its own. Heavy deposits of chromium of this type are referred to usually as "hard" chromium-plate for no very clear reason, since neither the methods of deposition nor the hardness of the deposit differ substantially from those employed in normal decorative chromium-plating; the sole difference is the thickness of coating applied.

Practically all present-day chromium-plating in this country is carried out from a solution of chromic acid containing a small but well-defined concentration of sulphate, generally sulphuric acid, although some sodium sulphate is occasionally used. The absolute concentrations of chromic acid and sulphate in the bath are of secondary importance to the main factor, which is the ratio of chromic acid to sulphate. This ratio is best maintained at about 100:1, the limiting ranges for deposition being within the approximate limits of 200:1 and 50:1. Outside these limits little or no chromium can be deposited from the solution.

Other acid radicals have been introduced, particularly chloracetic, hydrofluoric, or hydrofluosilicic acids, with or without sulphate; these are, however, not generally considered to have any notable advantages over the chromic acid-sulphate solution. To some extent, perhaps, the introduction of these solutions has been influenced by the fact that the chromic acid-sulphate solution has been protected by patents⁽¹⁾ in the United States, but not in Great Britain. On the

other hand, it is claimed by Fischer⁽²⁾ that a bath containing both hydrofluoric and hydrofluosilicic acids is stable and gives a higher current efficiency and harder and more lustrous deposits than those containing only sulphate. The chromium-plating patents have been the subject of considerable litigation.⁽³⁾

The Plating Solution.—Chromic acid is a strong acid and is supplied for plating purposes in the form of dark red flakes; it must be substantially free from excess sulphuric acid or sulphate because of the critical effect of the concentration of these acid catalysts on the operation of the solution. Two main types of solution are in common use—i.e. the concentrated bath and the dilute bath. A typical “concentrated” bath contains:

Chromic acid (CrO_3)	.	.	.	80 oz./gall.
Sulphuric acid (H_2SO_4)	.	.	.	0.8 oz./gall.

The dilute solution contains about half the above concentrations of these constituents, but almost any concentration of solution can be successfully employed above about 25 oz. gall. of chromic acid provided the correct chromic acid to sulphate ratio is maintained. In actual practice the intermediate concentrations are little used, for reasons which will become apparent.

The choice as to whether the concentrated or the dilute solution is to be employed depends on working conditions. The latter bath is naturally much more sensitive to changes in the sulphate ratio such as may be brought about by carry-over from acid dips or by depletion of the chromic acid by rapid working, since the solution is always operated with inert anodes. The dilute solution also has a lower conductivity, so that higher operating voltages are required to maintain an adequate working current density. On the other hand, such solutions have a higher cathode efficiency and a somewhat wider bright plating range. The last-named aspect will be discussed in greater detail later.

The high density solution containing 60 to 80 oz. gall. of chromic acid is more suited to really heavy production because of its higher conductivity and the fact that changes in solution composition are of less significance than is the case with the more dilute solutions. On the other hand, drag-out losses are necessarily higher with heavier solutions. This is usually not a serious matter, because it is the practice in chromium-plating, in view of the relatively expensive nature of the solution, to return the rinsing water to the plating tank for “make-up” purposes.

Chromic Acid Economy.—Chromic acid is an expensive material, so that careful attention should be given to reducing wastage as much as possible. In view of the fact that the loss of chromium from the bath by spray can be five to ten times as great as that deposited on the work, whilst the loss by drag-out is also very considerable, it is undoubtedly more economical to work with the low-density solution. Spray losses can be reduced by the use of small polystyrene or polythene tubes floated on the surface of the bath, or by regular additions of selected wetting agents. The former effect a considerable saving, but cannot be used satisfactorily in most automatic plants as the tubes are pushed to the end of the tank by the movement of the work, or where hollow work is being treated which will carry the tubes out of the solution. Wetting agents are slowly decomposed by the highly oxidising nature of the solution and may cause the trivalent chromium content to rise in time.

Drag-out losses can be reduced by the use of a drag-out tank for the first rinse, which should be agitated by air; when the chromic acid concentration in this tank has reached about 10 to 15 per cent of that of the plating bath it should be withdrawn and used for making up the main bath, either directly or after concentration by evaporation. According to Soderberg⁽⁴⁾ drag-out losses can be substantially reduced by: (1) withdrawing the parts slowly from the solution; (2) increasing the draining time above the tank; (3) keeping the withdrawal time as long as possible and the drainage time as short as possible for a given total drag-out time period; (4) racking so that the solution can flow off at a tip or corner, and that there are no horizontal surfaces or solution pockets; (5) preventing drip from one part flowing on to another.

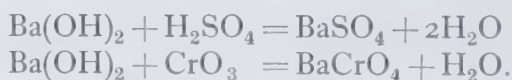
The low-density bath can give very satisfactory results if the temperature is raised to improve conductivity and if the sulphate ratio is raised to 120:1 or more to compensate for the reduced throwing power which results from the use of high temperatures and low chromium content.⁽⁵⁾ It is necessary to obtain the optimum ratio between the brown iridescent stain found at high ratios and the low throwing power at the low ratios.

Anode and Cathode Reactions.—In the course of plating, some of the hexavalent chromium content of the solution is reduced at the cathode to the trivalent form; although a degree of re-oxidation takes place at the anode, this is by no means complete, so that in due course trivalent chromium compounds (e.g. chromium sulphate, $\text{Cr}_2(\text{SO}_4)_3$, and chromium chromate, $\text{Cr}_2(\text{Cr}_2\text{O}_7)_3$), gradually accumulate in the solution. Some is lost by "drag-out", but the concentration

should not be permitted to become excessive, as trivalent chromium compounds have the effect of narrowing the bright plating range of the solution and decreasing its conductivity. On the other hand, a moderate concentration of trivalent chromium appears to increase the throwing power somewhat. Iron dissolved in the solution has a similar effect.

If the trivalent chromium concentration should become excessively high (more than about 8 oz. to 10 oz. per gallon), it is possible to promote its re-oxidation to chromic acid by passing current through the solution, using a lead cathode inside a porous pot.⁽⁶⁾ In this way oxidation of the solution at the anode proceeds whilst the reducing action at the cathode is inhibited. The process is, however, a very slow one if large volumes of solution are to be dealt with (cf p. 339).

Should it be desired to reduce the sulphate content, this is best carried out by the addition of barium hydroxide, $\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$. Rather more than the theoretical quantity of this compound may be required in order to precipitate the requisite amount of sulphuric acid. The theoretical proportion is 3.1 oz. of barium hydroxide for each ounce of sulphuric acid, but not all of the barium compound goes to the precipitation of barium sulphate, as some barium chromate is also formed:



The process is best carried out in a separate tank at a high temperature (about 75° C.) and the treated solution decanted off. A preliminary test of an aliquot portion of the solution will enable the correct amount of hydroxide required to be calculated.

Anodes.—The chromium content of the plating solution must be maintained by regular additions of chromic acid, and insoluble anodes of antimonial lead are usually employed. These may be flat sheets or of corrugated construction with cast-in copper or brass suspending hooks for maximum conductivity. Antimonial lead is preferable to pure lead because it is mechanically stronger and also resists the action of the solution better. Pure lead is more resistant to the electrolyte than antimonial lead during the passage of current, but is markedly inferior when electrolysis is not proceeding. The resistance of antimonial lead to chemical dissolution by chromic acid increases with increasing antimony content, the usual proportion of antimony being about 5 per cent. Tellurium-lead anodes containing about 0.2 per cent of tellurium have also shown certain advantages.

while more recently the use of tin-lead alloys has been recommended as withstanding the solution more satisfactorily.⁽⁷⁾ In operation the lead anodes become coated on the surface with a chocolate-brown layer of lead peroxide, which has the effect of re-oxidising any lower oxides of chromium that may be produced in the solution to the hexavalent state. This reduction to trivalent chromium takes place continually, and, as has already been stated, excessive concentrations lead to reduced efficiency of the bath. If the anode area is insufficient, the rate of formation of trivalent chromium will tend to be increased. The anodes, may, moreover, become overheated with the high current densities used, and will then disintegrate more readily. In the absence of the peroxide film the anodes become coated with lead chromate as a result of attack by the chromic acid. This film (unlike the lead peroxide) is non-conducting and must be scraped off from time to time. The lead peroxide film can be re-established, if necessary, by working the anodes for a time in a dilute solution of sulphuric acid. By correct operating conditions the rate of formation of lead chromate can be markedly reduced so that only infrequent cleaning of the anodes will be needed. This anode reaction is an essential part of the chromium-plating process. For this reason chromium anodes could not successfully be used, even if they were available at an economic price, since they would be unable to oxidise the chromium chromate formed at the cathode to chromic acid so that the electrolyte would soon become unworkable. A further objection to the use of chromium anodes is the fact that the anode efficiency of the solution is about ten times as great as the cathode efficiency, so that the metal content of the bath would build up at an inordinate rate.

The anode to cathode ratio is of importance in reducing the tendency for trivalent chromium salts to build up in the solution. The anode area should in no case be less than the cathode area, but the exact ratio depends a good deal on the conditions of operation. Anode cathode ratios of 2 or 3 to 1 have been employed.

PLANT

Chromic acid solutions are highly oxidising in character, and readily oxidisable materials must not be employed in contact with them. Tanks are generally made of steel, which usually has an internal lining of antimonial lead. Steel tanks with an inner loose glass lining have also been used, but this arrangement is much less satisfactory, as the steel dissolves in the solution to some extent. Lead-lined plant lasts very well, and as steel is only slowly attacked

by chromium-plating solution local failures in the lead lining do not immediately cause serious failures. It is best to suspend an inner lining of wired or armoured glass sheets inside the tank to minimise the risk of short circuits with the anodes or the work during operation. Some use of acid-proof brick linings inside steel tanks has also been reported from the U.S.A. for chromium-plating tanks.

Rubber-lined tanks cannot be used with chromic acid but vinyl



Fig. 99.—Automatic chromium-plating plant for cycle parts

[Courtesy of Hercules Cycle Co. Ltd., and W. Canning & Co. Ltd.]

co-polymers withstand the acid well. The plastic lining is applied in sheet form and bonded to the steel tank; such linings have given very satisfactory service.

Chromic acid solutions attack copper only very slowly, so that copper bus-bars are employed for connections and for the wiring-up of small parts. Copper wire mesh trays or baskets can also be used for dealing with very small articles.

Heating.—Heating is carried out by means of lead-covered coils in the solution, or, better still, by iron coils in an outer water-jacket surrounding the tank containing the chromic acid solution. This latter arrangement is much to be preferred, because a greater uniformity of temperature can be maintained. The high density of the chromic acid bath makes it difficult to prevent temperature variations within the solution in the absence of a water-jacket. Close

temperature control is essential if bright deposits are to be consistently obtained. Owing to the high currents used, considerable heat is developed in the solution, so that heating is usually only required when the plant is being started up. In many large plants, therefore, cooling coils are installed in the water-jacket in order to keep the temperature of the bath from rising excessively when the plant is being operated continuously for long periods at a time.

Automatic Plant. Although a great proportion of the chromium-

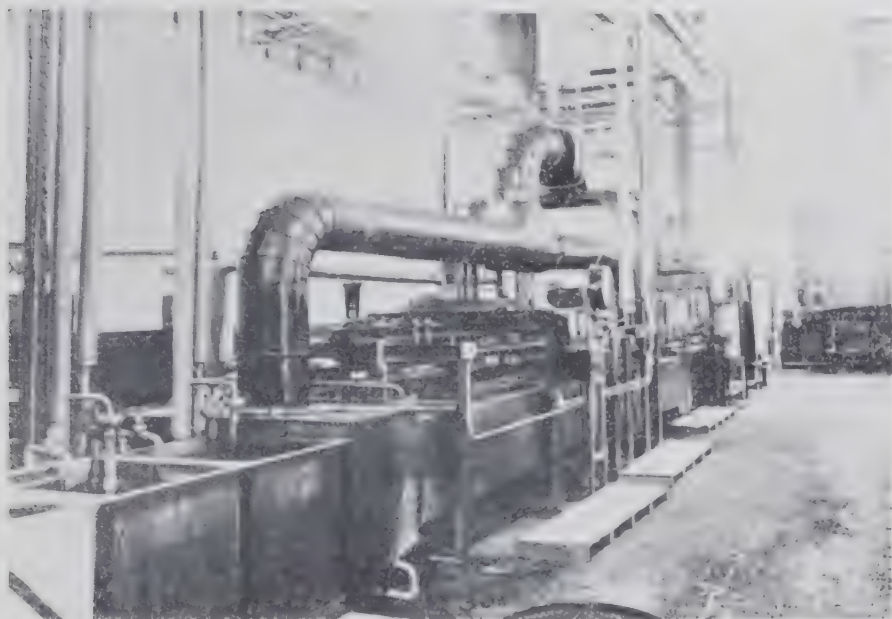


Fig. 100.—Semi-automatic rotary chromium-plating plant

[Courtesy of W. Canning & Co. Ltd.]

plating carried out in this country is done in manually operated plants, various types of automatic units have been designed, and these present many advantages. Fig. 99 shows a fully automatic straight through plant complete with wash tanks, etc., for the chromium-plating of cycle parts. In Fig. 100 a semi-automatic rotary plant is illustrated. The components here travel continuously around the plant, so that only one operator is required, as there is only one loading and unloading point. Rinsing is done by hand. The slow movement of the work through the solution helps deposition considerably. Combined automatic bright nickel and chromium-plating installations have been introduced in recent years and have given very satisfactory service; plants of this type have been described. (See p. 251.)

Fig. 101 shows an ingenious automatic plant for the chromium-plating of steel parts, such as automobile hub-caps. Racks are dispensed with, the articles being held on to the periphery of the slowly moving ebonite-covered wheels magnetically. This type of plant is only suited for very short plating times, as for longer times the discs become of unwieldy dimensions.

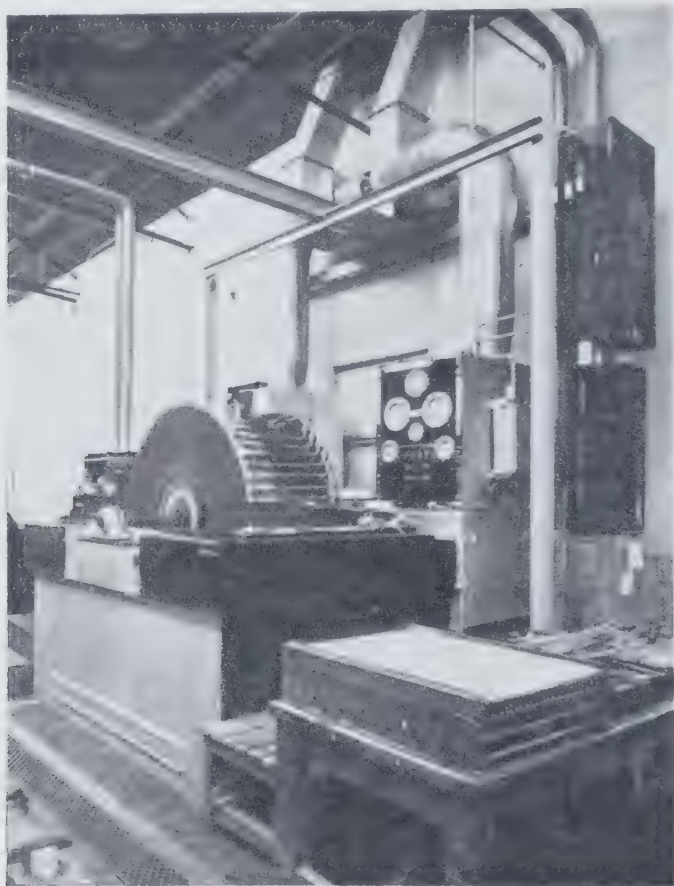


Fig. 101.—Rotary automatic chromium-plating plant with magnetic work attachments

[Courtesy of the Electrochemical Engineering Co. Ltd.]

Barrel Chromium Plating.—A great deal of attention has been given to the problem of chromium-plating small parts in a barrel. This presents considerable difficulties on account of the narrow bright plating range of the solution, its poor throwing power and the need for good electrical contact.

In one type of unit which has been found useful for a range of small components such as nuts and bolts and small fittings generally, the parts are fed from a hopper into a small barrel where they are

plated and then automatically discharged for rinsing, neutralising and drying (Fig. 102). The electrolyte used is the hydrofluoric acid type, a chromic acid content of 200 to 300 gm. l. being used with a hydrofluoric acid addition of 1 to 2 per cent. The bath is operated at about 90° F. An applied potential of 6 to 8 volts is required.

For satisfactory plating, the articles should not be allowed to stand



Fig. 102.—Barrel chromium plant

[Courtesy of the Electrochemical Engineering Co. Ltd.]

for a long period after nickel-plating. Even so, the operation is likely to result in a substantial proportion of the parts failing to plate properly over their full surface or with milky patches at high-current density areas. For this reason barrel chromium-plating is only suitable for small parts where the standard of inspection is not too critical. More recently a measure of success has been achieved by a horizontal type of partially immersed barrel into which the work is directly loaded (Fig. 103). The form of the barrel is such that an opening on its periphery acts as a chute into which the articles to be plated are loaded. After plating, the barrel is then transferred mechanically to

the drag-out tank, where rinsing is carried out; it is then rotated in the reverse direction, whereupon the plated articles are discharged from the chute into a tray fitted near the top of the tank. Heating is by means of a water-jacket, and a 500-ampere rectifier supplies the current. It is claimed that this barrel will plate one quart of articles

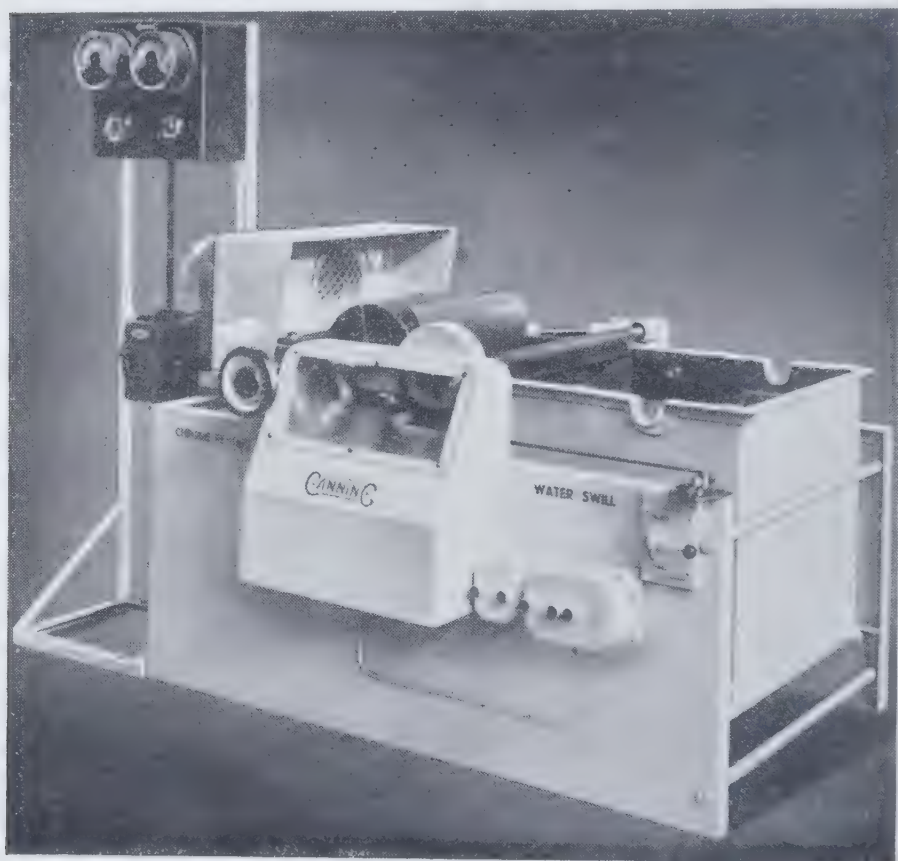


Fig. 103.—Barrel chromium plant

[Courtesy of W. Canning and Co. Ltd.]

up to 1 in. in diameter, or pins, bolts, etc., up to 2 in. long in ten minutes.

Exhaust Equipment.—In the course of chromium-plating large volumes of oxygen and hydrogen are liberated because of the low cathode efficiency of the solution. This carries into the air a considerable amount of chromic acid spray, which is highly irritant to the mucous membranes of the nose and throat and can cause ulceration and even perforation of the nasal septum unless precautions are taken to prevent its entry into the atmosphere.

In the early days of chromium-plating, the tank was often fitted with lids, or a layer of paraffin oil was kept on the surface of the solution in an attempt to prevent liberation of spray. Nowadays cross-ventilation of the tank is employed, the spray being extracted by exhaust fans. Fans and duct-work can be satisfactorily constructed from steel sheet, preferably treated with a bitumen-based paint to minimise attack by the solution. Drain-off valves must be provided

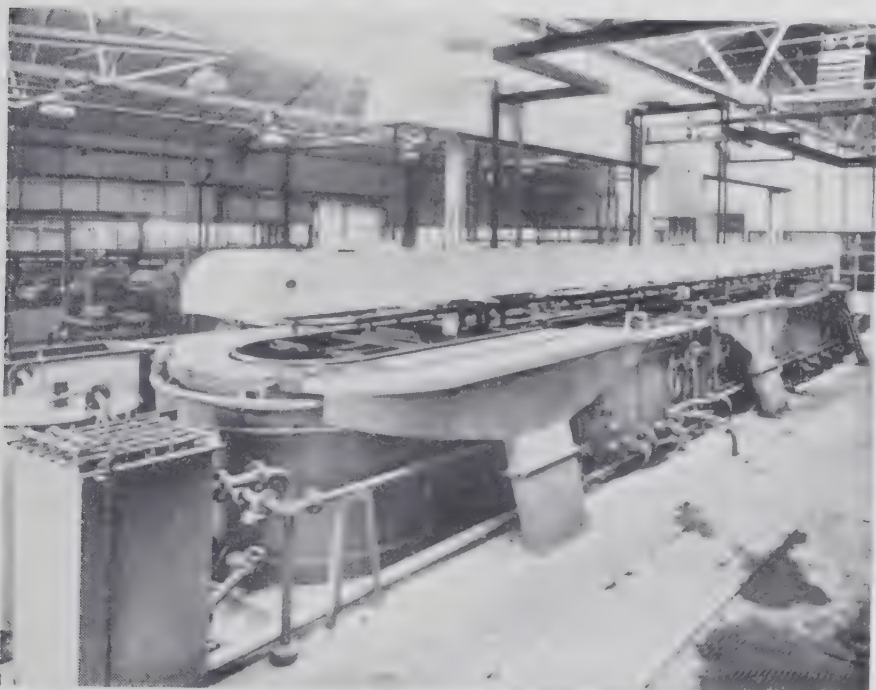


Fig. 104.—Automatic plating showing arrangement of exhaust ducting
[Courtesy of the Electrochemical Engineering Co. Ltd.]

at the lowest points of the exhaust installations to enable the condensed spray to be drawn off from time to time. If an adequate rate of air-flow is employed (about 2,000 ft. per minute) little spray enters the atmosphere. The above-mentioned rate of extraction, if applied by means of a slot along one side of the tank, is sufficient for a bath about 24 in. wide. Wider tanks are best dealt with by slots along both sides. Alternatively, it is preferable to extract even narrower tanks by means of exhaust slots along two sides. The level of the solution should be kept about 9 in. to 12 in. below the top of the tank to keep the spray from rising unduly. If possible, the best arrangement is to lead the exhaust ducting down below ground level as in the case of the automatic plant shown in Fig. 104. A recent

improvement has been the use of a layer of small plastic tubes floated on the surface of the bath; these tubes prevent the spray from rising mechanically and reduce chromic acid losses considerably. They are of less value in automatic plants as they tend to be carried forward in the direction of movement of the work. Certain wetting agents are also commercially available which reduce losses by lowering the surface tension of the solution. They are, however, slowly oxidised by the chromic acid and must be constantly replenished. Chromic acid is also irritant to the skin, and good washing facilities must be provided for operators. Dermatitis and ulcers which are difficult to heal are especially prone to occur if the acid is allowed to enter abrasions in the skin.

Insulation.—Rack insulation is very important in chromium-plating, as the metal is somewhat costly and it is desirable to conserve power as far as possible owing to the poor cathode efficiency of the solution. Ebonite-covered racks have had a measure of success, as have coating varnishes based on polyvinyl resins. Waxes, especially chlorinated naphthalene waxes, are valuable in "stopping-off" areas which are not to be plated, especially in heavy chromium-plating for engineering applications.

Temperature.—Owing to the extreme hardness of chromium deposits and the consequent difficulty of polishing them, it is desirable to produce bright coatings directly from the solution, if possible. This is of no great consequence where heavy deposits are being applied for industrial purposes, but is important in the case of thin coatings applied for protection against tarnish. Generally speaking, with the usual types of solution already described the bright plating range is a function of the temperature and the current density, higher temperatures being required for the higher current densities. If the temperature is too low for the current density being employed, the deposits are milky or frosted in appearance and can only be polished with difficulty, if at all. If the current density is higher still, "burnt" deposits will be obtained which are rough or nodular and may be dark in colour. Conversely, if the temperature is raised whilst the cathode current density remains unchanged, the efficiency falls rapidly until deposition is inhibited altogether.

The decrease in cathode efficiency with rise of temperature means that in order to obtain bright deposits some reduction in cathode efficiency must be expected. Bright deposits cannot readily be produced at temperatures below about 80° F. or at current densities of less than about 40 amps. per sq. ft.

The ranges within which various types of deposit are obtained

from a solution of 250 gm. l. of chromic acid and 2.5 gm./l. of sulphuric acid are shown in Fig. 105(8).

Fig. 106 shows the densities of solutions containing varying concentrations of chromic acid at 25° C. This provides a simple means of testing the strength of a bath by means of a hydrometer, but in the case of old solutions the curve is subject to modification, due to the presence of trivalent chromium, iron, etc.

Efficiency and Current Density.—The efficiency of the chromium-plating solution, even under the best conditions, is very low. It is highest when the bath is operated cold, and efficiencies

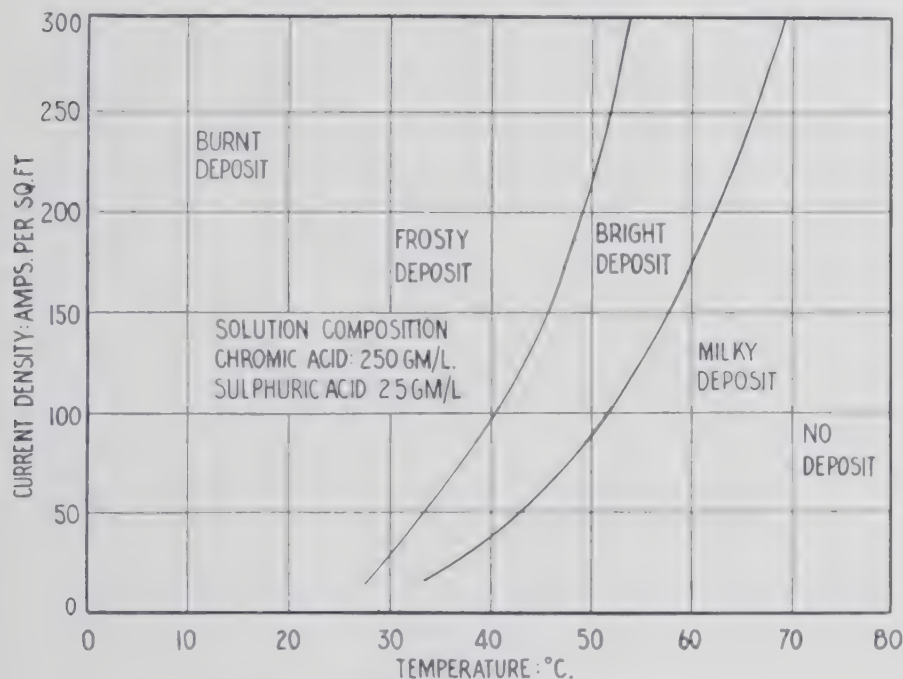


Fig. 105.—Plating range of low density chromium solution

of 35 to 40 per cent can then be obtained. The deposits under these conditions are, however, hard and frosted in appearance. Within the bright plating range—i.e. at temperatures of about 100° F. to 110° F.—the efficiency is much lower and does not usually exceed 10 to 15 per cent. In commercial plating it is usually necessary to plate irregularly shaped articles, so that it is desirable to work with a solution having a wide current density range, in order that a bright deposit may be obtained on all significant surfaces; hence the ratio of the minimum to the maximum current densities within which bright deposits are obtainable should be as high as possible.

Current densities of 100 to 200 amps. per sq. ft. are most commonly employed in practice, the voltages usually needed being 5 to 8 volts with low-density solutions or 4 to 6 volts with the more conducting high-density solutions. The high currents used mean that large-capacity generators or rectifiers are necessary, whilst

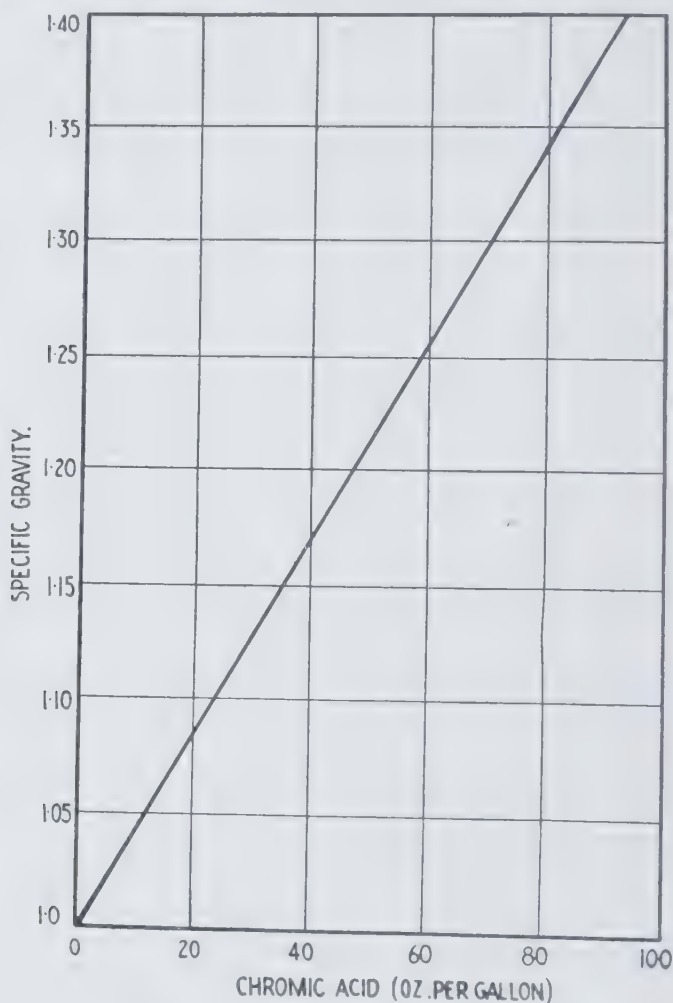


Fig. 106.—Densities of chromic acid solutions

plating racks and wires must be of ample dimensions to carry large currents. A good guiding rule is to allow 1,000 amps. per sq. in. cross-section of copper conductor.

Dubpernell⁽⁹⁾ has studied the rate of deposition of chromium from solutions containing 250 gm. l. and 400 gm. l. of chromic acid respectively, with a chromic acid/sulphate ratio of 100:1 in each case. The current efficiencies were determined on flat poles under

accurately controlled conditions to ensure uniform current distribution over the entire surface in each case. Figs. 107 and 108 show the rates of deposition from these two solutions. In actual practice, however, these rates of deposition are not always maintained, and some variation from them is to be expected in the case of articles of complex shape.

Throwing Power.—The throwing power of chromium solutions is very poor, and in some instances auxiliary anodes in the form of

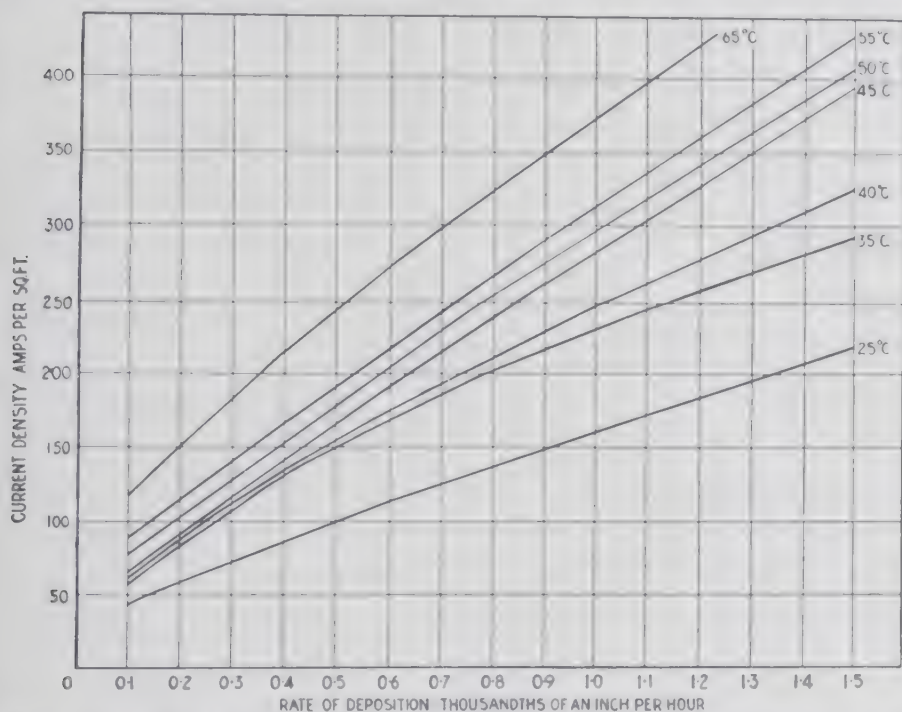


Fig. 107.—Rate of deposition of chromium from low density solution. CrO_3 ; 250 gm./l. H_2SO_4 ; 2.5 gm./l.

lead strips or wires may be necessary to enable recessed areas to be covered. Again, owing to the low efficiency of the solution, large volumes of gas are evolved, and if the articles being plated contain holes, the stream of gas bubbles liberated will effectively prevent deposition over an area around them. Such holes are therefore best plugged during plating.

The throwing power is, again, unfortunately reduced by the elevated temperatures required for bright plating, the cold solutions giving matt deposits having the best throwing power. On the other hand, for a given temperature increased throwing power is obtained by increasing the current density, and it is therefore desirable to

work at as high a current density as possible within the bright-plating range if the best "throw" is to be obtained. It has also been stated that the low-density solutions have better throwing power than have those of high density, while high sulphate ratios favour increased throwing power.

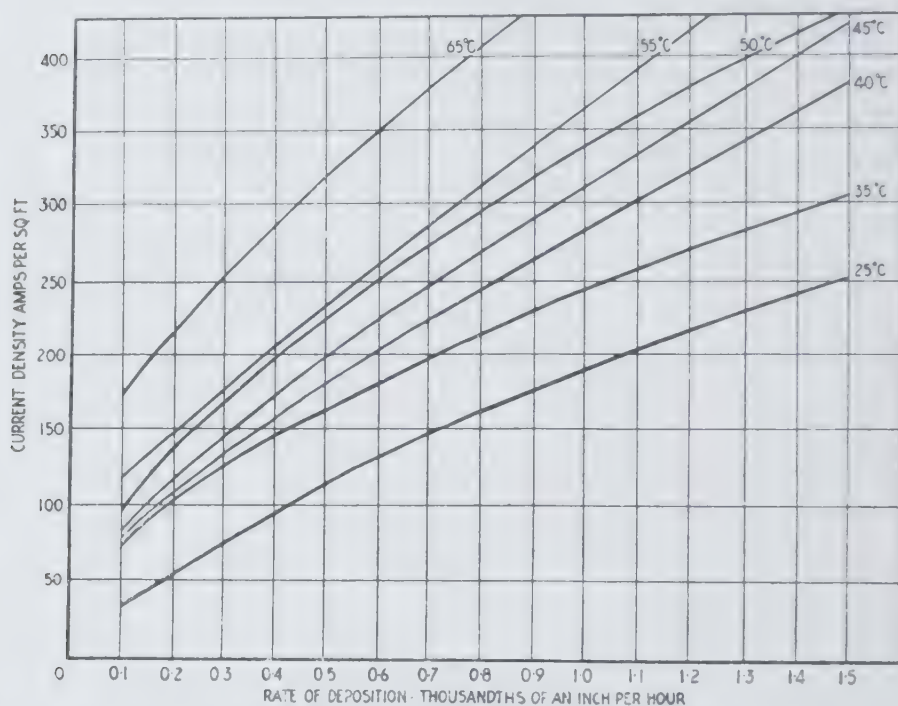


Fig. 108. Rate of deposition of chromium from high-density solution. CrO_3 , 400 gm./l. H_2SO_4 , 4 gm./l.

Defects in Chromium-plating.—Amongst the commoner defects in chromium-plating practice are:

- Streaked deposits.*—This shows itself in the form of white or milky streaks on the plated surface and is usually the result of plating at too low a current density.
- Matt deposits.*—The bath temperature should be increased to eliminate this defect.
- Thin or discoloured deposits.*—These may be due to excessive bath temperatures which lower the rate of deposition. The sulphate ratio can also cause discolouration, a low ratio giving a yellowish deposit.
- Burnt deposits* are the result of too high a current density, and can be corrected either by reducing this or by the use of shields at edges or corners.

- (e) *Unplated areas.*—These are usually the result of gas liberation preventing deposition on certain zones. Careful attention to racking position in relation to holes and recesses in the article being plated will correct this condition.

Pre-treatment before Chromium-plating. The chromic acid solution, being highly oxidising, is capable of plating on to metal surfaces which are slightly greasy and not so meticulously free from foreign matter as is necessary for the deposition of most other metals. Also the considerable amount of gas which is liberated during plating serves to break up any slight films which may remain. Nickel deposits after polishing can usually be directly chromium-plated without any cleaning, provided too long an interval does not elapse between finishing and plating. In handling articles between these operations for wiring or racking it is desirable that the operator wear cotton gloves, as finger-marks may in some cases show through the chromium-plate. After nickel finishing, a wipe with a dry buff and a little lime suffices to produce a surface clean enough for direct plating, whilst larger surfaces are sometimes cleaned more thoroughly by means of a rouge paste or an organic solvent.

The formation of dull spots or streaks on the surface of the chromium-plate is often due to the presence of an oxide film on the underlying nickel. This may be occasioned by undue delay between polishing and chromium-plating, or may be caused by excessive heating during the polishing operation. Such heating is more likely to occur on components of thin section, which attain high temperatures more rapidly than do heavier articles during buffing.

Electro-alkaline cleaning, followed by a dilute sulphuric acid dip prior to chromium-plating, is not often used, but a good case can be made out for its introduction in large-scale production. Such cleaning can do much to minimise the incidence of chromium-plating defects caused by surface contamination with grease or polishing composition, or resulting from slight surface oxidation. If this procedure is employed, very efficient rinsing arrangements are necessary, owing to the extreme sensitivity of the plating solution to the sulphate radical; where the articles to be plated are so constructed that thorough removal of traces of acid cannot be effected, wet-cleaning methods of this description are best avoided. Indeed, the problem of acid removal is often an extremely difficult one to solve even under good conditions of rinsing.

Bright nickel deposits are sometimes inclined to be "passive", especially if any appreciable period elapses between nickel- and

chromium-plating. Unplated areas may then manifest themselves on the articles when they are withdrawn from the plating tank. In such cases "activation" by a dilute acid dip or by electrolytic treatment in a cyanide solution is recommended.

Rinsing.—After chromium-plating, it is usual to have two cold rinses, followed by an alkaline neutralising tank containing a dilute sodium carbonate solution, and then a further cold rinse and a hot-water tank for drying off. In the case of large articles drying may be difficult, and water stains may then be left on the work, so that sawdust or oven-drying has to be resorted to. Infra-red ovens have proved useful for this purpose in some instances.⁽¹⁰⁾

Thickness of Deposit.—For the normal production of nickel- and chromium-plated ware, such as in the case of motor-car accessories, bathroom equipment, etc., the chromium deposits as generally applied do not exceed 0.00001 in. to 0.00002 in. in thickness. The latter thickness is the minimum coating needed to comply with the British Standard Specification (B.S.S. 1224 : 1945). Such deposits are mainly applied to protect the underlying metal from tarnish; their intrinsic corrosion-preventing qualities are not very great. Chromium deposits are highly stressed, and as the thickness increases, fine cracks tend to develop which diminish the protective value of the coating. With greatly increased thicknesses, however, these cracks are built over, and although new cracks are formed in turn, these will not then extend through to the base metal. In fact the appearance of the surface of a heavy chromium deposit under the microscope has been described as being similar to that of a mudflat baked in the sun. The use of heavy coatings is, however, confined to industrial applications for wear-resistance and anti-friction properties, as they are relatively expensive to apply and to finish. For this reason decorative plating processes do not as a rule make use of greater thicknesses of chromium than about 0.00002 in., usually applied over a nickel undercoat. Deposits of greater thickness than this (apart from heavy deposits) have inferior protective value, and may also be rather difficult to polish.

A further point in connection with chromium-plating is that the highly stressed nature of the deposit imposes a severe test on the adhesion of the underlying nickel. The adhesion of deposits under chromium must be of a high order, or "blistering" will occur during chromium-plating. Increasing the thickness of chromium again increases this stress, so that heavier deposits of chromium call for even better nickel adhesion than do the lighter deposits.

Effects of Impurities.—The chromium solution, being highly

corrosive, tends to accumulate foreign metallic ions very readily, due to attack on work passing through, on racks, anodes, connecting bars, tanks, etc. The commonest of these extraneous constituents are iron and copper. Trivalent chromium compounds also build up in the solution, and the influence of these has already been pointed out. In general, the presence of such cations has an undesirable influence on the solution, decreasing its conductivity, although it has been claimed that zinc improves the efficiency. The presence of excessive amounts of iron is known to reduce the bright plating current density range of chromium solutions.

Removal of Trivalent Chromium.—Trivalent chromium compounds are, however, the most common source of trouble in chromium baths; these compounds are formed rapidly at high anode current densities such as occur when hollow parts are plated with auxiliary interior anodes especially.

Recently the conditions for the re-oxidation of trivalent chromium have been worked out, and it is claimed that under the appropriate conditions such re-oxidation can be achieved without the use of a porous diaphragm around the cathode.⁽¹¹⁾ Electrolysis should be carried out at a high temperature (about 180°F.) at a high current density, such as 560 amps. per sq. ft., and a low anode current density of about 20 amps. per sq. ft. The cathode surface is a small round steel rod, the anode area being about thirty times as great as the cathode. Lead or antimonial lead anodes are used. It is not necessary to remove the sulphate from the solution.

Under these conditions with a solution containing 250 gm. l. of chromic acid and 2.5 gm. l. of SO_4 ion, 22 hours are required to reduce the trivalent chromium content from 22 to 5 gm. l. These figures are based on a current volume ratio of 5 amps. per gallon.

The mechanism of the chromium-plating reaction has been the subject of some controversy, in particular as to whether the chromium is deposited directly from the hexavalent state or from the trivalent salt. It has now been incontrovertly proved that the metal is deposited directly from the hexavalent state. This fact was established by the use of radio-active chromium 51 as a tracer element in the plating solution.⁽¹²⁾

Properties of Electro-deposited Chromium.—Chromium, as deposited, is a bluish-white metal which has highly non-tarnishing qualities. As is to be expected, its reflectivity in the blue region of the spectrum is good, but over the entire visible range the reflectivity appears to be about 65 per cent. Bright chromium deposits have a hardness range of 400 to 1,200 Brinell, depending on the conditions

of deposition. According to Cymboliste, the hardness varies with current density, temperature, chromic acid concentration, and the presence of different anions and cations.⁽¹³⁾ The crystal structure influences the hardness and the general properties of the resulting

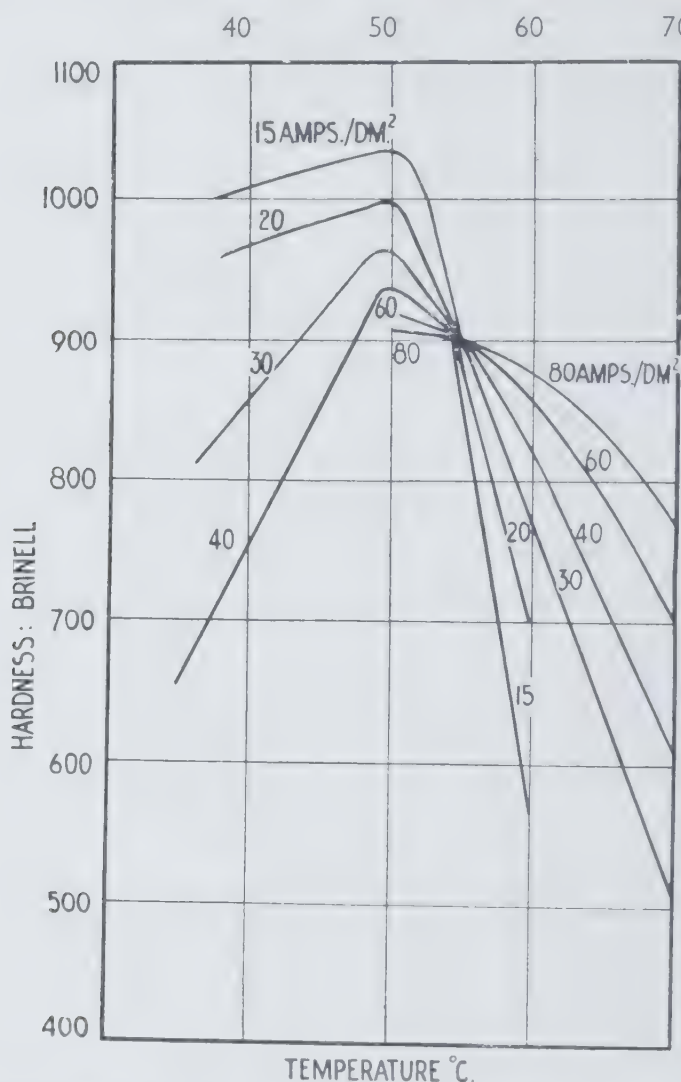


Fig. 109. —Effect of plating temperature on hardness of electro-deposited chromium

deposits. Cymboliste also found that for a concentration of 300 gm. l. of chromic acid and a sulphate ratio of 50:1 an increase in current density reduced the hardness of chromium-plate at temperatures below about 55° C., and increased it at temperatures above this figure. For all current densities the maximum hardness appears to be

obtained at bath temperatures in the neighbourhood of 50 C.; the effect of the plating solution temperature on the hardness of the deposit obtained from this bath is shown in Fig. 109. This work does not distinguish between dull and bright deposits; the hardness

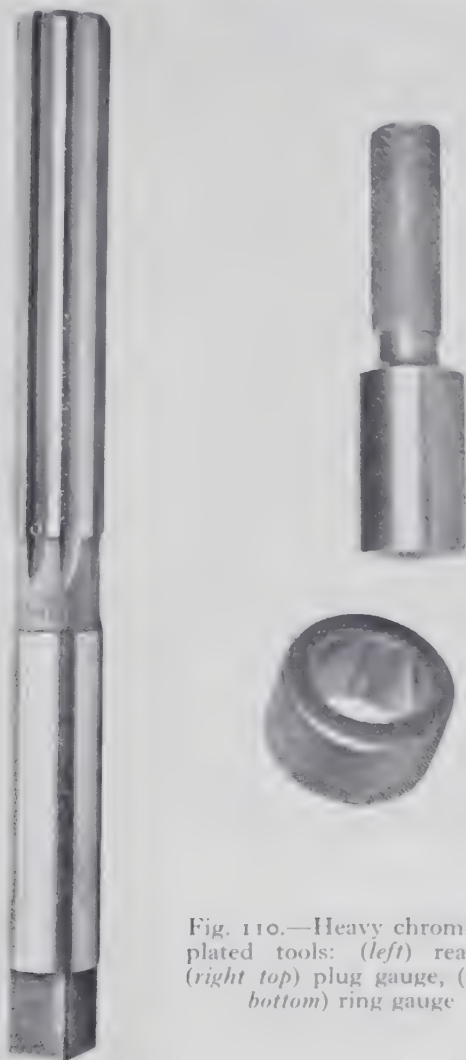


Fig. 110.—Heavy chromium-plated tools: (*left*) reamer, (*right top*) plug gauge, (*right bottom*) ring gauge

of the bright range of deposits as obtained from warm solutions appears to be in the region of 800 to 900 Brinell.⁽¹⁴⁾ The hardness of all types of electro-deposited chromium is much greater than that of the cast metal. On annealing the electro-deposited metal, the hardness appears to decrease until values as low as 70 to 90 Brinell are obtainable.⁽¹⁵⁾

For bearing surfaces chromium deposits have the great advantage in addition to their hardness of having the lowest coefficient of friction of any other metal combination.

Hard Chromium-plating.—In recent years a considerable amount of attention has been given to hard chromium-plating for wear resistance, and a large number of papers have appeared on the subject. Although this aspect of chromium deposition is outside the scope of the present book, the subject is so important as to merit notice here. Chromium deposits of 0.001 in. or more in thickness are usually covered by the term "hard" chromium-plating, and such deposits are regularly applied to dies, moulds, tools of various kinds, etc., to increase their life and to provide smoother and longer wearing surfaces. Some typical hard-chromium-plated tools are shown in Fig. 110. The chief advantages of the use of such coatings are their hardness, corrosion resistance, and low frictional characteristics. The processes of deposition are similar to those already described, but special precautions are necessary in the pre-treatment prior to plating, to ensure that good adhesion is obtained to the base metal.⁽¹⁶⁾ The latter should also be of adequate strength, to prevent failure of the tool due to underlying weakness of the base metal. In particular, proper heat-treatment is essential to relieve stresses and strains which would otherwise be accentuated by plating.

Usually steel is cleaned in an alkaline bath and then anodically etched in sulphuric acid or chromic acid solutions at not too high a current density. This provides a good key for the subsequent deposit, since the character and grain size of the plate are determined by the condition of the steel base. Baking after plating at a temperature of 350° F. to 400° F. is advisable to relieve the hydrogen embrittlement of the deposit and to increase the ultimate strength of the chromium-plated part. Chromium is also applied to build up worn parts, whereby a new lease of life is given to shafts, cylinders, etc.

Although chromium deposits can sometimes be applied of sufficiently accurate thickness to eliminate the need for subsequent grinding, very often such grinding, with or without subsequent lapping, may have to be carried out in order to obtain the required dimensional limits.

Recently porous chromium deposits have been introduced, and such coatings appear to have greater wear-resisting properties than the normal type of dense chromium deposits, owing to their oil-retaining qualities.⁽¹⁷⁾

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- (17) H. Van der Horst, *Met. Fin.* (1942), **40**, 69.

CHAPTER X

COPPER AND BRASS DEPOSITS

COPPER-PLATING

Copper is deposited for four main purposes:

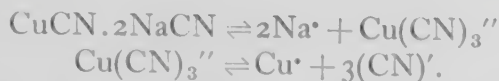
- (a) As an undercoat for nickel in the plating of metals, such as zinc-base alloy die-castings to prevent attack on the zinc by the nickel solution. Copper undercoats are employed sometimes prior to the nickel-plating of steel, either to reduce polishing costs or to improve the corrosion resistance of the coatings.
- (b) In the production of bronze finishes on steel and other metals; the parts are first copper-plated, after which the copper is coloured by some such treatment as immersion in sulphide solutions.
- (c) For the local protection of steel during case-hardening.
- (d) In electro-forming and in the production of printing plates by the electrotpe process.

SOLUTIONS

Only two types of solution are used on any large scale—i.e. the cyanide and the acid solutions. The first type consists essentially of a solution of cuprous cyanide in an alkali metal cyanide with or without various addition agents. Cyanide solutions have excellent throwing power; they are, however, unsuited, in general, to the building up of deposits of substantial thickness, but have the advantage of being directly applicable to ferrous metals. The acid solution consists of a solution of copper sulphate and sulphuric acid, and is used mainly for plating on to those metals which are not attacked by the solution chemically, and especially where substantial thicknesses are required, as in electro-forming. It is not possible to plate on to steel or on to zinc alloys from the acid solution.

The alkaline cyanide copper bath is employed when steel or zinc are the basis metals, since the copper is in the form of a complex anion and deposition by immersion does not take place. This type of solution is employed almost exclusively where copper is required as an undercoat prior to nickel-plating. The cyanide solution

consists essentially of a solution of copper cyanide in sodium or potassium cyanide together with an excess of cyanide (the "free" cyanide content). The double cyanide of copper is formed in the solution ($\text{CuCN} \cdot 2\text{KCN}$ or $\text{CuCN} \cdot 2\text{NaCN}$). Dissociation of this double cyanide occurs:



The second stage of dissociation only takes place to a very small extent, so that the concentration of cuprous ions in the solution is very small. As deposition proceeds, however, further dissociation takes place so that the concentration of copper ions in the solution is maintained. Rolled, extruded, or cast copper anodes are employed. Cast anodes are the least satisfactory, owing to the possible presence of occluded oxide particles, which may lead to sludge formation and consequent rough deposits.

A typical solution consists of

Copper cyanide, CuCN	.	.	4 oz./gall.
Sodium cyanide, NaCN	.	.	6 oz./gall.
Sodium carbonate, Na_2CO_3	.	.	2 oz./gall.

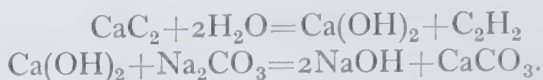
Since the formation of the double cyanide requires 1.093 lb. of NaCN for every 1 lb. of CuCN , this allows for approximately 2 oz. per gallon of "free" cyanide.

Operation.—The solution is normally operated at about 90 F. to 100 F., with current densities of up to 20 amps. per sq. ft. As the solution ages and the carbonate content rises it is necessary to increase the free cyanide content to maintain anode corrosion and to decrease anode polarisation. Excessive cyanide results in a high rate of hydrogen evolution with a consequent lowering of current efficiency, and may cause blistered deposits.

When the carbonate content becomes very high (e.g. 6 oz. or more per gallon) it is desirable to remove the excess either by discarding a portion of the solution or, better, if the equipment is available, by freezing to slightly below 0 C., when most of the carbonate will crystallise out.

A novel method for the removal of excess carbonate has been recommended by Ross.⁽¹⁾ In this method 0.6 oz. gall. of calcium carbide is added for each 1 oz. gall. of carbonate. The carbide reacts with the water to form calcium hydroxide, which in turn precipitates

the sodium carbonate as calcium carbonate. The acetylene which is liberated is removed by the exhaust.



Some free carbon and sulphides are also precipitated from impurities in the carbide, but can be removed by decantation or filtration. Too much carbide should not be added at once to avoid increasing the pH of the solution unduly rapidly.

The calcium carbide should be added in small amounts sufficient to give the desired free caustic soda content; it is best carried out on part of the solution in a separate tank from which the sludge can be removed by decantation and washed.

Calcium sulphate in a finely divided form can also be employed for carbonate removal. The amount required is 1.6 times the weight of sodium carbonate to be removed.

The use of more concentrated solutions has been advocated by Pan⁽²⁾ and by Young and Reid⁽³⁾ with copper contents of 12 oz. or more per gallon; such solutions operate at greater current efficiencies. It is claimed that with solutions of this type current efficiencies of up to 95 per cent can be obtained at 20 amps. per sq. ft. at room temperature. The tendency is nowadays to use solutions with higher metal content.

Cyanide solutions are commonly worked in steel tanks, although more recently rubber-lined tanks have been increasingly employed to prevent iron contamination. Iron entering the solution cannot be readily removed, and has been shown to reduce the efficiency of the solution.⁽⁴⁾

Since the copper ions in the cyanide solution are part of a complex ion the actual concentration of metal ions in the bath is extremely small. This has the effect of producing an extremely fine-grained deposit which is columnar in nature. This, however, renders the structure of the deposit very sensitive to the presence of inclusions, and where these occur the grains tend to grow radially from the inclusion so that a nodule is formed. A nodule can actually originate at any nucleus which is sufficiently large to interrupt the growth of the grain, so that new grains originate from this nucleus generally in the form of a conical group with a rounded top. Naturally in baths producing deposits of coarser grain it will need a larger-sized inclusion to have a similar effect; for this reason it is easier to produce a smooth heavy deposit of copper from an acid copper sulphate bath than from a cyanide solution.

The Rochelle Salt Solution.—Increasing interest has been taken in recent years in cyanide copper solutions containing appreciable concentrations of Rochelle salt (sodium potassium tartrate). It is well known that in the ordinary cyanide solution raising the metal content and lowering the free cyanide enables higher current densities and better efficiencies to be obtained, especially if the bath is operated at an elevated temperature. Unfortunately, however, anode corrosion tends to be poor under such conditions, and anode films form; the addition of Rochelle salt seems to result in the

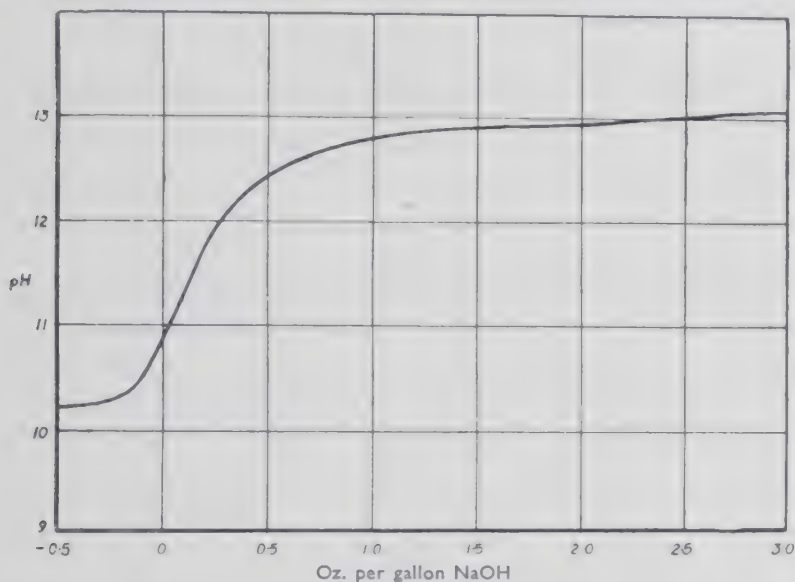


Fig. 111.—Effect of caustic soda additions on the pH of Rochelle salt copper solutions

elimination of such anode films and good anode corrosion is obtained, so that higher current densities can be employed.

According to Wagner and Beckwith,⁽⁵⁾ the optimum concentration of Rochelle salt is 3.8 oz. gall., the efficiency falling at higher concentrations. It is, however, usual to work with larger amounts to make up for loss through drag-out in the course of operation. Carbonate is added to reduce anode polarisation and to stabilise the pH value, which is controlled by the addition of caustic soda (see Fig. 111). A pH value of 12.2 to 12.8 is considered to give the best plating conditions; the lower value is difficult to maintain, as the solution is poorly buffered, so that it is general to work within a pH range of 12.5 to 12.8. At too high a pH value, the anode efficiency is considerably reduced. A further advantage of lower pH values is that in the difficult operation of copper-plating on zinc-base die-castings

it has been shown by Maher⁽⁶⁾ that the tendency to "blistering" is progressively reduced as the pH decreases.

A recommended Rochelle salt bath consists of:

Copper cyanide (CuCN)	. . .	4½ oz./gall.
Sodium cyanide (NaCN)	. . .	6 oz./gall.
Rochelle salt ($\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$)	. . .	7½ oz. gall.
Sodium carbonate	. . .	2½ oz./gall.
Free NaCN	. . .	1 oz./gall.
pH	. . .	12.6
Temperature	. . .	140° F. to 160° F.

An increase in free cyanide, like the addition of caustic soda, results in increased conductivity; unfortunately, however, increased gassing also occurs with high cyanide concentrations, leading to reduced current efficiencies. Trisodium phosphate acts as a buffer in small amounts at pH values below 12.2. Sulphites and thio-sulphates commonly added to ordinary copper cyanide solutions are undesirable in the Rochelle solution, as they may lead to the formation of anode films. The carbonate concentration builds up in due course, especially at high working temperatures, and when the concentration reaches 15 or 20 oz. gall. the solution may either have to be partly discarded or the carbonate crystallised out by refrigeration, if available, as with normal cyanide solutions. Chemical methods for the precipitation of excess carbonate are not to be recommended for this bath.

High temperatures favour high efficiencies, but temperatures in excess of 160° F. are not practicable owing to the high rate of decomposition of the cyanide; at temperatures above 140° F. exhaust equipment is necessary in view of the fumes evolved. Under these conditions, current densities as high as 60 amps. per sq. ft. can be successfully employed with cathode efficiencies approaching 70 per cent.

The anode current density must also be carefully controlled, and it is desirable to have an anode area equal to twice the cathode area at least. The free cyanide content must be controlled by regular analyses and kept as low as possible consistent with the maintenance of film-free anodes.

Periodic filtration is helpful in maintaining a smooth and non-porous deposit, but, as in the case of practically all cyanide solutions, a degree of roughness accompanied by a tendency towards blister formation develops if an attempt be made to build up thicknesses much above 0.001 in. Contamination of Rochelle copper solutions

with hexavalent chromium compounds is a danger, particularly where automatic plants are used. The effect of these compounds is to cause a reduction in efficiency with the formation of streaked deposits. Treatment with sodium hydrosulphite, $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, is an effective method of purification, the chromium being reduced to the trivalent state and precipitated.⁽⁷⁾

Chevreur's Solution.—This solution is not very extensively used nowadays, but it does give smooth deposits and has had considerable commercial application. Chevreul's salt is cupric cuprous sulphite, $\text{CuSO}_3 \cdot \text{Cu}_2\text{SO}_3 \cdot 2\text{H}_2\text{O}$, and a suitable solution may be made up by dissolving $4\frac{1}{2}$ oz. of Chevreul's salt together with $5\frac{1}{2}$ oz. of sodium cyanide in a gallon of water. The cyanide should be dissolved first. The solution is worked at a temperature of about 120°F ., under similar current density conditions to those used in the cyanide solutions previously described. Too high current densities lead to dark brown, rough and burnt deposits; this can be corrected by the obvious method of using lower current densities or by increasing the temperature of the bath. The free cyanide content must be controlled so as to keep the anodes just free from green deposits, avoiding an excess. As has already been stated, the exact amount depends on the carbonate concentration. (See p. 345.)

Pyrophosphate Solutions.—Recent developments have included work on solutions based on pyrophosphates and such baths have had some commercial application. Both sodium and potassium baths have been described, a typical solution consisting of:

Copper pyrophosphate $\text{Cu}_2\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$	110 gm. l.
Potassium pyrophosphate $\text{K}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$	404 gm. l.
Ammonia (0.880 sp. gr.)	3 gm./l.
Citric acid	10 gm./l.

Operating Conditions

pH	8.5
Temperature	120°F .
Current density	5 to 50 amps./sq. ft.

The molar ratio of pyrophosphate to copper should not exceed 2 : 1 as too much pyrophosphate decreases the current density range. The current density permissible can be increased by elevating the temperature and by means of agitation. Lactic, fluoboric or malic acids have been recommended as brighteners for use in the above bath. The pyrophosphate solutions have been employed to produce

a smooth and readily buffed copper deposit on steel as an undercoat for bright nickel.

A further development by Stareck(*) has been the addition of nitrates to the pyrophosphate bath, whereby it is claimed that improved stability up to the boiling-point can be obtained, together with a greatly increased plating rate and a softer and more ductile deposit. This bath is suitable for barrel plating, "striking", and plating on to aluminium alloys and stainless steel.

Orthophosphate Bath.—Recent investigations suggest that an orthophosphate copper can give good deposits.⁽⁹⁾ Such a bath is made up most simply by dissolving copper oxide in phosphoric acid and adding sulphuric to adjust the pH to the optimum value of 0.5. A considerable amount of acid is required as the solution is highly buffered. A preferred formula is:

Copper oxide, CuO	. . .	93 gm./l.
Phosphoric acid (sp. gr. 1.7)	. . .	500 gm./l.
Sulphuric acid (sp. gr. 1.86)	. . .	37 gm./l.
Gelatine		0.05 gm./l.
Allylthiourea		0.2 gm./l.

The pH is 0.5 and the operating temperature is 30° C. Current densities of 15 to 50 amps. per sq. ft. can be safely employed without agitation, but with agitation higher figures can be used. Anode and cathode efficiencies approach 100 per cent. The bath cannot be used for direct plating on ferrous metals.

Without the addition agents ductile, smooth deposits are produced which are easily buffed, but by the addition of gelatine and thiourea mirror-bright deposits are said to be obtained. As compared with the sulphate bath, the solution gives brighter deposits at higher current density ranges, but its throwing power is poorer, its limiting current density is lower, and its cost is higher.

Copper Sulphamate.—Sulphamate solutions have been used for the deposition of copper. The metallic salts of sulphamic acid ($\text{HSO}_3\cdot\text{NH}_2$) are stable and soluble, and it is claimed that metals such as iron, nickel, cobalt, cadmium, rhodium, silver, lead and zinc can be successfully deposited from sulphamate baths. One solution for copper is comprised of:

Ammonium sulphamate ($\text{NH}_4\cdot\text{SO}_3\cdot\text{NH}_2$)	100 gm. l.
Copper sulphate ($\text{Cu SO}_4\cdot 5\text{H}_2\text{O}$)	. 130 gm. l.
Sodium hydroxide NaOH	. . . 7.5 gm./l.

Current densities of up to 35 amps. sq. ft. can be employed.

Addition Agents.—Small concentrations of sodium thiosulphate or sodium sulphite are often added to cyanide copper solutions to improve the brightness of the deposits, but excessive amounts must be avoided or decomposition of the additive to the sulphide may occur with the formation of dark and brittle deposits. In the case of copper deposits applied to zinc-base alloys as an undercoat for nickel, it is found that a high degree of visual brightness does not always typify the best undercoat for successful bright nickel-plating; very often a copper deposit which appears quite dull to the eye will be more satisfactory if it is fine-grained.

High-speed Cyanide Copper Solutions.—Considerable interest has been aroused in the U.S.A. by cyanide solutions which, it is claimed, will operate at high speeds and efficiencies, and will enable heavy deposits to be built up directly on steel, for example, without recourse to an acid copper sulphate solution (p. 355). One improved copper bath which gives good results has been described in some detail,⁽¹⁰⁾ and consists of a solution of the double cyanide of copper and an alkali metal to which is added not less than 1 oz. per gallon of potassium sulphocyanide, together with about 0.1 oz. per gallon of a soluble carbohydrate such as wheat starch, mannite, molasses, etc. At temperatures of 60°C. to 90°C. smooth lustrous deposits are claimed at current densities of 10 to 30 amps. per sq. ft.

More recently the characteristics of an American commercial high-speed solution have been described.⁽¹¹⁾ The principles on which this solution is based are: (i) the use of a high concentration of sodium cuprous cyanide; (ii) low "free" cyanide; (iii) a relatively high sodium or potassium hydroxide content; (iv) high operating temperature; (v) suitable brightening and anti-pitting agents; (vi) electrode film replenishment by agitation.

Bath Composition.—The solution composition is given as:

Copper cyanide (CuCN)	. . .	120 gm./l.
Sodium cyanide (NaCN)	. . .	135 gm./l.
"Free" NaCN	. . .	3.75 gm./l.
Caustic soda (NaOH)	. . .	4 gm./l.
Anti-pit agent	. . .	0.2 gm./l.
Brightener	. . .	2 gm./l.

The brightener preferred is potassium sulphocyanide again, the anti-pitting agent being a betaine, a cyclic amine containing one non-cyclic hydrocarbon radical of 10 to 20 carbon atoms. Another type of addition agent is the cyclic methylene ether of piperonal which may be used in conjunction with a soluble molybdenum compound.

More recent developments indicate that superior results can be obtained by the addition of certain quaternary ammonium compounds such as trimethylbenzyl ammonium chloride in the proportion of 0.2 to 0.6 oz. per gallon, together with betaine-type compounds in amounts of 0.012 to 0.12 oz. per gallon, to cyanide-plating solutions. The ammonium compounds prevent the formation of films which are only removed with difficulty when betaine-type compounds are used alone.⁽¹²⁾ These additions are especially suitable for high-efficiency baths in which there is no visible hydrogen evolution, and they also minimise the effects of harmful contaminants.

As much as 60 gm. l. of carbonate formed by absorption of carbon dioxide from the atmosphere can be tolerated, whilst the substitution of potassium cyanide for the sodium cyanide in the solution enables current densities of up to 100 amps. per sq. ft. to be employed at 100 per cent cathode efficiency. Simultaneously the copper content can be reduced to about half of that quoted above.

The solution is operated under the following average conditions:

Cathode current density	.	.	50 to 60 amps. sq. ft.
Anode current density	.	.	Not more than 30 amps./sq. ft.
Temperature	.	.	170° F. to 180° F.

It is claimed that both anode and cathode efficiencies are approximately 100 per cent, and in consequence of this little or no decomposition of cyanide takes place, despite the high operating temperature. Such decomposition normally occurs as a result of the reaction:



The authors claim that, in the main, the oxygen required for this reaction to occur is provided in the course of electrolysis, so that if anode efficiencies are maintained at 100 per cent cyanide decomposition does not take place.

Agitation of the cathodes, preferably with solution circulation, is required to permit the use of high cathode current densities. Within given limits the current density range in which bright deposits are obtained varies directly with the speed of cathode agitation. The optimum rate of agitation is 8 to 12 ft. per minute.

PERIODIC REVERSE CURRENT

The use of various forms of alternating current in plating processes has been practised for very many years; in particular alternating current superimposed on direct current has been proposed as a means

of increasing the rate of deposition. The method of periodic reversal which is now used on a fairly large scale, particularly in the U.S.A., was first proposed by Jernstedt in 1948. It is most useful in the case of cyanide solutions and has been employed commercially in the deposition of copper, zinc, cadmium, silver, brass and gold. Essentially the process consists in reversing the current periodically, using a relatively slow cycle. The exact PR cycle used is determined by experiment in each case, but the most common cycle is one of 20 seconds plating followed by 5 seconds deplating at very high current densities.

By the use of periodic reverse current plating there is much less tendency for nodule formation, building up at corners and edges, roughness, and similar defects which often result when any attempt is made to deposit considerable thicknesses of metal at high current densities, to occur. This is because the momentary deplating process removes foci from which nodulation develops. It is claimed that by PR plating methods smooth deposits up to one-quarter inch thick can be produced quite free from nodules and of a high degree of uniformity even on corners and edges. Deposits of up to 0.001 in. in thickness can be obtained fully bright whilst the levelling action of the process can often result in the surface being smoother than the base metal.

Although the PR current process obviously has a lower efficiency per cycle than normal direct current plating, the high current densities which can be employed means that the overall plating time for a given thickness of deposit can be substantially reduced. The process is a flexible one, smoothness increasing with the proportion of the total cycle time during which deplating takes place.

Equipment.—The methods employed for effecting current reversal are of the utmost importance for the successful operation of the process. Switching must be rapid, as if the current does not build up to its full value at each reversal the rate of deposition will be greatly reduced, whilst the deposit may be of poor appearance. When a motor generator is used as the source of current a timer either of the electronic or mechanical type is employed to reverse the field excitation of the generator or to switch a current reversing contactor on the generator output side. The former method is simple to execute, but is not suitable unless the period of reversal is at least 5 seconds.

When rectifiers are used low voltage contactors on the output side may be similarly employed. When large currents are to be reversed, it is better to use a double system in which a small high-voltage

contactor breaks the circuit on the A.C. input side whilst a larger contactor reverses the current on the low-voltage side.

For the optimum result the plating solutions used should be specially selected for the method. Organic addition agents are best avoided, but some inorganic additives are useful, particularly in copper baths. Copper solutions are most commonly used with this method, as it enables heavy and smooth deposits to be produced at current densities of up to 200 amps. per sq. ft. or even more. These deposits are particularly suitable as undercoats for nickel deposits on steel.

Blistering of Copper Deposits.—Copper undercoatings are extensively applied to zinc-base die-castings prior to nickel-plating, since such plating cannot be successfully carried out directly on to zinc unless special nickel solutions having severe limitations are employed. There is no commercial bright nickel-plating solution which can be used directly on zinc-base alloys. Only a thin copper deposit (about 0.0003 in. thick) is usually required.

One of the main difficulties with the copper-plating of zinc-base alloys is a tendency for "blisters" to form in the deposit usually after nickel-plating, even when quite thin deposits are applied. (See p. 293.) The cleaning procedure to be applied to zinc before plating must be carefully selected to prevent action of the cleaner on the metal. Mild alkalis, such as trisodium phosphate, must be used, and over-cleaning avoided; it has been shown by Oplinger⁽¹³⁾ that over-prolonged alkaline or acid treatment prior to plating increases the tendency for "blistering" to occur. Cathodic alkaline cleaning is also more likely to cause blister formation than anodic cleaning.⁽¹⁴⁾

A recent detailed study of the problem of blistering⁽¹⁵⁾ based on potentiometric measurements suggests that when zinc-base die-castings are subjected to cathodic alkaline cleaning, or even to alkaline cleaning without the use of current, the aluminium-rich portions of the alloy tend to go into solution at a much greater rate than the zinc-rich portions. This tends to form pits on the surface, which at times may extend through the denser surface layer into the sub-surface cavities, forming small channels leading into these internal cavities. Alkaline solution is trapped in such pores and concurrently loosely adherent gelatinous aluminium hydroxide, a loosely adherent zinc deposit, and deposits of other more noble metals present in the alloy may be formed on the surface. The trapped solution reacts with the basis metal under the plating, producing hydrogen gas, which in turn lifts the deposit.

The Fluoborate Bath.—The copper fluoborate bath has found increasing application because of its good stability, high anode and

cathode efficiencies (approaching 100 per cent), and the smooth and ductile deposits obtained from it without the use of addition agents.

The copper fluoborate is best obtained as a concentrate which is then diluted to the appropriate volume. It contains free fluoboric and boric acids. A suitable bath contains about 300 gm. l. of copper fluoborate, $\text{Cu}(\text{BF}_4)_2$, and is operated at a temperature of 90° F. to 100° F. and a pH of 0.5 to 0.7. Air agitation or cathode-rod movement can be used with advantage. For barrel plating, bath concentrations 50 per cent or more higher than this can be used. The pH of the solution can be raised by means of copper carbonate or lowered by the addition of fluoboric acid. Periodic filtration through activated charcoal is helpful, but paper filters or silica-type filter-aids should be avoided. The pH is important, since if this rises too high the deposits will be dark and brittle, whilst too low a pH results in a reduced permissible cathode current density.

Rolled or electrolytic copper anodes are recommended. Nylon or other synthetic fibre anode bags are helpful in preventing a reddish-brown powder which sometimes forms on the anode from entering the bath.

Other Solutions.—Other types of copper-plating solutions have been recommended from time to time, such as thiosulphate solutions containing cuprous chloride,⁽¹⁶⁾ and the triethanolamine solutions containing sodium oxalate and copper sulphate,⁽¹⁷⁾ but these have not been employed on any scale. The only other important solution is the acid copper sulphate bath.

The Acid Copper Solution.—Acid copper-plating is carried out from a solution consisting fundamentally of copper sulphate and sulphuric acid. The solution is simple and inexpensive to prepare and the anode and cathode efficiencies generally approach 100 per cent. Thick deposits can be built up which are highly adherent at considerable current densities. The deposit from this type of solution is usually matt and requires considerable buffing if a bright surface is required. Recently, however, various bright acid copper baths have been developed; these will be referred to later.

Much more careful cleaning of the base metal is required before acid copper-plating than is the case with cyanide solutions, since, unlike the latter, the sulphate solution does not possess detergent properties.

The usual range of composition of this type of solution is:

Copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	25 to 35 oz. gall.
Sulphuric acid	8 to 12 oz./gall.

A high concentration of metal is desirable. The presence of sulphuric acid in the solution lowers the solubility of the copper sulphate, however, so that the concentration must not be so high that crystallisation will take place. The effect of sulphuric acid on the solubility of copper sulphate in water at 25° C. is shown in Fig. 112. The presence of sulphuric acid is essential, as it prevents the formation of precipitates of basic copper salts and also increases the conductivity of the solution, thus lowering power costs. By reducing the concen-

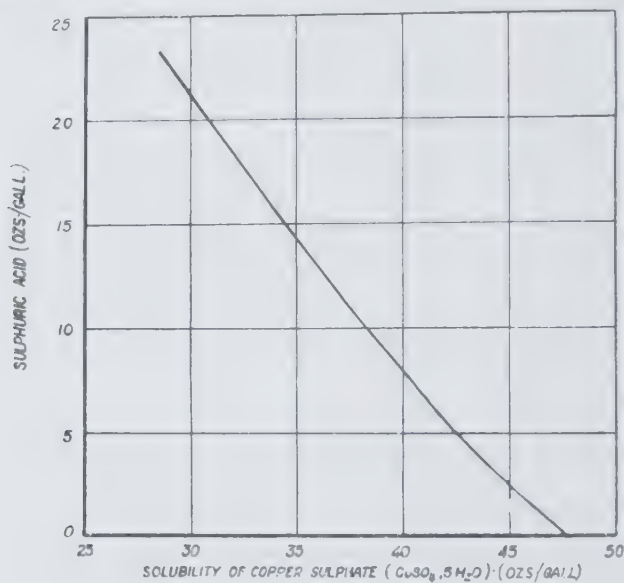


Fig. 112.—Effect of sulphuric acid on solubility of copper sulphate at 25°C.

tration of copper ions in the solution the acid also has the effect of producing smoother deposits of small grain size.

Operating Conditions.—Current densities of 20 to 60 amps. per sq. ft. are commonly employed, although under special conditions very much higher current densities can be used. Suitable conditions can be arranged in automatic plants, where a substantial degree of movement of the cathode relative to the electrolyte can be obtained. Copper solutions are usually operated at room temperature, although sometimes temperatures as high as 120° F. are employed. Elevating the temperature results in a softer copper deposit, as does likewise an increase in the metal content of the solution or a decrease in the sulphuric acid concentration. Air agitation increases the current density which can be employed without “burning” or “treeing”, but the use of agitated copper solutions is by no means universal in electro-plating practice.

Addition Agents.—Various materials are added to the solutions with the object of obtaining deposits of greater smoothness, glue and dextrin being amongst the commonest additions. Glue particularly tends to counteract the tendency for “treeing” to occur and results in smoother deposits. Very small concentrations only should be used (e.g. 0.001 oz. gall. or less). Excessive concentrations can cause dark or brittle deposits, which can be troublesome, especially when electro-forming is being carried out. For the production of soft and ductile deposits it is essential, however, that the bath be free from organic contaminants.⁽¹⁸⁾

Bright acid solutions, using molasses and thiourea as addition agents, have also been described and have received some commercial application in the U.S.A.⁽¹⁹⁾ A typical composition used in production is:

Copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	. 210 gm./l.
Sulphuric acid	. 30 gm./l.
Molasses	. 0.80 gm./l.
Thiourea	. 0.04 gm./l.
Temperature	. 70° F.
Current density	. 50 to 70 amps./sq. ft.

The addition of a surface agent (Triton No. 720, a salt of a sulphonated ether) helps to produce a soft semi-bright deposit. The lustre falls off at temperatures above 80° F., while excessive concentrations of addition agent may cause “orange-peeled” or striated deposits.

Phenolsulphonic acid as an addition agent has been recommended for producing fine-grained smooth deposits, by Hull and Blum.⁽²⁰⁾ This compound is produced by treating phenol with an equal weight of concentrated sulphuric acid, and is used in the proportion of 1 gm. per litre of solution.

The use of iron in the acid solution has been recommended, it being claimed that current densities as high as 280 amps per sq. ft. can be obtained from solutions containing 20 g. l. of ferrous iron.

Tanks.—Acid copper solutions were formerly almost exclusively operated in lead-lined wood tanks, but more recently rubber-lined steel has found extended application because of the many advantages which such equipment offers. The outside of the tank should receive treatment with an anti-sulphuric asphaltic paint, because the solution is highly corrosive.

Stoneware and laminated plastic composition tanks have also been employed, but to a lesser extent.

Cuprous Acid Solutions. Acid copper solutions have the disadvantage of producing relatively large-grained deposits as has already been indicated, whilst their throwing power is also poor. Owing to the fact that the copper is in the form of a divalent ion, more power is also required for a given amount of deposition than is the case from the cyanide bath. Attempts have been made to overcome these disadvantages by the use of cuprous acid solutions and two have been recommended, viz.: (a) cuprous chloride and (b) cuprous chloride-sodium thiosulphate solutions. These solutions are said to give bright deposits, but have the disadvantage that the cuprous compound tends to oxidise unless special precautions are taken, as by the use of a small amount of sodium bisulphite in the bath, or by working with a layer of paraffin on the solution.

Amine Baths.—Another solution which has had some application in the U.S.A. is the amine-type of bath, which enables bright copper deposits of considerable thickness to be built up.⁽²¹⁾ Copper plated from this type of bath can be used as an undercoating for bright nickel on zinc-base die-castings or on steel provided a thin flash of copper from a cyanide solution is first applied.

For average conditions the following is recommended:

Copper sulphate	.	.	.	.	20 oz./gal.
Diethylene triamine	.	.	.	.	16 oz./gal.
Ammonium sulphate	.	.	.	.	3 oz./gal.
Ammonia (sp. gr. 0.88)	.	.	.	.	5 oz./gal.
Wetting agent (Tergitol 08)	.	.	.	.	0.4 oz./gal.
pH	.	.	.	.	9.0 to 10.0

The solution should be filtered through activated clay and plating carried out on dummy cathodes at a low current density before use.

Ammonium sulphate and ammonia are essential for bright plating, a high ammonia content being desirable where high current densities are used. Burning and pitting are indicative of low ammonia.

The wetting agent reduces the tendency for pitting to occur, but its presence is not essential if the solution is properly filtered and well agitated. The pH should not be allowed to fall too low or the deposit will be dark in colour; too high a pH on the other hand results in a dull plate. The recommended current density range is 30 to 50 amps. per sq. ft., with a temperature of 120° F. to 140° F.

Direct bright nickel-plating can be carried out, but it is essential to prevent any carry-over of the solution since amines in a nickel bath cause severe embrittlement of the nickel. The solution tolerates zinc well, but iron, lead and organic impurities cause rapid loss of

brightness. This sensitivity to contaminants is a serious disadvantage of the solution.

For smooth deposits it is necessary to maintain the solution substantially free from dust and suspended matter, and in this connection periodic filtration is helpful. Usually the metal content of the solution tends to rise during operation, while the acid concentration falls. This is caused by slight chemical dissolution of the anodes whereby there is a tendency for the copper to pass into solution in the form of cuprous ions to some extent; these are oxidised to the cupric stage, increasing the copper content of the solution. This oxidation may even cause the precipitation of finely divided metallic copper either on the anodes or within the solution. Build-up of the metal content can be minimised by replacing some of the copper anodes by anodes of an inert metal—e.g. lead. If lead anodes are not employed, part of the solution must be discarded from time to time. Rolled or cast copper anodes, preferably oval in shape, are most generally employed, both for cyanide and acid solutions, the former being the more satisfactory. The anode area should be approximately equal to that of the cathode. Too high an anode area will result in excessive anode dissolution.

Electro-typing and Electro-forming.—Copper deposition is widely used in the preparation of moulds for various purposes, especially for printing. Rotary printing machines use electrotypes on a large scale. A form is first produced from some such material as a wax composition, plaster of Paris, etc., which is then rendered non-porous by treatment with a suitable lacquer or varnish. The mould is then rendered conducting by the application of a film of graphite or bronze powder whilst the lacquer film is still tacky, after which it is plated in the usual manner in an acid-copper solution. Modern electro-forming technique is described in detail by Winkler.⁽²²⁾

Other commercial applications of acid copper-plating which do not come within the scope of the present volume are the manufacture of electro-formed reflectors for searchlights, etc.,⁽²³⁾ and the production of copper powder by an electro-plating technique which results in the formation of a highly brittle, easily pulverised deposit. Thin copper sheet has also been produced on a commercial scale in this country by a continuous electro-plating process in thicknesses of from 0.003 in. to 0.02 in., and in rolls 4,000 to 5,000 ft. in length and 64 in. wide.⁽²⁴⁾ The process is, however, rather difficult to operate, particularly from the point of view of maintaining a uniformly thick deposit.

Copper deposits are also employed on a large scale in the selective carburising of steel parts. In the carburising process areas which are to be kept soft are given an electro-deposited coating of copper, which must be of adequate thickness and non-porous. This protects the underlying steel locally from the action of the carburising compound.

BRASS-PLATING

The electro-deposition of brass is to-day an important industrial process. The commonest brass deposit is the alloy with a 70:30 copper-zinc ratio; this brass has a distinctive yellow colour which is a useful criterion for judging whether the correct composition is being maintained. Brass-plating is applied for decorative purposes, whilst its attractive appearance also makes it useful for the protection of steel fittings and similar articles for service under indoor conditions. The protection afforded by a brass deposit against corrosion is not high, so that it is not suited for outdoor exposure.

A most important application of brass-plating is in the bonding of rubber to steel; an extremely strong bond is obtained when rubber is vulcanised on to the brass-plated metal. The bond is stronger than that obtainable by any other method, and is, in fact, greater than the strength of the rubber itself.

Bonded rubber of this type finds extensive uses in engineering for flexible and anti-vibration mountings, couplings, etc.

Solutions Used.—The standard type of brass-plating bath contains copper and zinc in the form of cyanides, the relative concentrations of the two metals being approximately the same in the solution as in the alloy which it is required to deposit. A typical brass-plating bath of this kind is as follows: (25)

Copper cyanide, CuCN	.	.	26.2 gm./l.
Zinc cyanide, Zn(CN)_2	.	.	11.3 gm./l.
Total cyanide	.	.	45.0 gm./l.

This bath is operated at a current density of up to about 10 amps. per sq. ft. Current densities in excess of this cause a marked reduction in cathode efficiency. The pH used lies between 10.3 and 11.0. In general, increasing the pH seems to increase the percentage of zinc in the deposit, but, on the other hand, lower pH values increase the current efficiency.

The pH may be controlled by means of caustic soda and sodium bicarbonate. The addition of caustic soda raises the pH whilst the bicarbonate lowers it. Brass anodes containing about 70 per cent of

copper and 30 per cent of zinc are employed. The anode and cathode efficiencies are relatively low, i.e. about 75 per cent. Anode corrosion is good, whilst the throwing power and conductivity of the solution are also reasonably satisfactory.

A certain amount of free cyanide (7 to 10 gm. l.) is essential in the solution to promote anode corrosion, but this should be kept low or the cathode efficiency will be adversely affected. On the other hand, if the cyanide is too low poor adhesion and blistered deposits result.

Temperature.—The temperatures used generally in brass-plating practice are of the order of 80° F. to 95° F.; raising the temperature tends to increase the cathode efficiency and permits higher current densities to be employed. Excessively high temperatures result in cyanide decomposition and rapid build-up of carbonate in the solution.

Ammonia is commonly added to brass solutions to improve the colour of the deposit, although ammonia and ammonium salts are normally liberated in the bath during decomposition of the cyanide. It is, however, difficult to maintain an adequate concentration, especially at high temperatures, in the usual type of bath without periodic additions of ammonia. The ammonia prevents any change in the proportion of zinc in the deposit which tends to decrease when the current density and temperature are raised in the absence of sufficient ammonia.

Rapid Plating Baths.—More recently, the technique of rapid brass-plating has been studied primarily for the purpose of applying 70:30 brass deposits to steel shell-cases.⁽²⁶⁾ The solution ultimately developed for this purpose consisted of:

Zinc cyanide, $\text{Zn}(\text{CN})_2$	.	.	54 gm./l.
Copper cyanide, CuCN	.	.	21 gm./l.
Sodium carbonate	.	.	20 gm./l.
Free cyanide	.	.	4 to 8 gm./l.
pH (Tropæolin "o")	.	.	12.6 to 12.8

This solution contains 30 gm. l. of zinc and 15 gm. l. of copper, which is approximately in inverse ratio to the composition of the deposit. It is thus seen that in this respect it differs fundamentally from the kind of solution hitherto used for the deposition of 70:30 brass. As has been stated, the usual methods for increasing the cathode efficiency at high current densities result in an increased copper content of the deposit, and this can be countered by the use of addition agents, especially ammonia. In the above solution,

however, the same result is obtained by reducing the concentration of copper ions relative to that of zinc ions.

This bath has been used on a large scale and has given highly satisfactory results. The cathode efficiency is 55 to 60 per cent at a current density of 20 amps. per sq. ft. and a temperature of 55° C. to 60° C. Under these conditions a deposit of 0.0003 in. can be applied in about twenty minutes. At higher temperatures the copper content increases and the deposit darkens in colour. No ammonia is added to the bath as the ammonia resulting from the decomposition of the cyanide is adequate for maintaining the conditions for good deposition. The stable concentration of ammonia is said to be 0.265 gm./l. The solution is best operated in a hard rubber-lined steel tank, but an iron tank with an inner glass lining can be employed.

An alternative solution in which reliance is not placed on the ability of the bath to generate and maintain its ammonia content has also recently been described, in addition to the above-mentioned high zinc ratio bath.⁽²⁷⁾

This bath is made up as follows:

Copper cyanide, CuCN	.	.	21 to 35 gm./l.
Zinc cyanide, Zn(CN) ₂	.	.	63 to 103 gm./l.
Sodium cyanide	.	.	83 to 131 gm./l.
Free cyanide	.	.	6 to 9 gm./l.
pH	.	.	10.5 to 11.5

Working Conditions—

Temperature	.	.	40° C. to 60° C.
Cathode current density	.	.	10 to 30 amps./sq. ft.
Cathode efficiency	.	.	60 to 90 per cent
Anode current density	.	.	5 to 10 amps./sq. ft. (max.)

The presence of ammonia in the bath to the extent of 0.8 to 1.0 gm. l. is essential to control the zinc content of the deposit, but no deliberate additions need normally be made to the bath as sufficient is generated to maintain an adequate content.

Dichromate Dip.—A dip in a 5 per cent solution of sodium dichromate after plating is useful in preventing staining of the deposit and especially in preventing dark-coloured spots due to traces of residual cyanide. This dip is not desirable if rubber bonding is to be carried out on to the brass. In this case the brass deposit should be washed and dried and the rubber bonding carried out with the least possible delay.

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THE DEPOSITION OF TIN AND ITS ALLOYS

Tin-plating is a process which presents many advantages for a variety of applications, especially in the food industry, because of the non-toxicity of the metal and its excellent resistance to alkalis and detergents. Tin coatings are also useful on parts which have to be soldered. The largest application of tin coatings is in the manufacture of tinned steel sheet for the canning industry and other purposes; while such sheet is still largely produced by hot dipping, an increasing amount of tin coating of sheet is being carried out by electro-deposition, particularly in the U.S.A. Refrigerator parts, dairy utensils, kitchen fittings, and numerous domestic accessories, are regularly electro-tinned. The protective value of tin coatings is also useful on non-ferrous metals—e.g. brass. On steel, tin is less protective than zinc or cadmium because of its cathodic characteristics relative to the base metal.

Tin is deposited from three main types of solution: (a) the chloride bath; (b) the stannate bath; (c) the acid tin bath. The first of these is now obsolescent, but is mentioned because it is still in current use to a limited extent.

The Chloride Bath.—The chloride solution is made up from stannous chloride and caustic soda, and consists essentially of a solution of sodium stannite containing an excess of free alkali. A typical bath⁽¹⁾ is made up from:

Stannous chloride, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	. 30 gm./l.
Sodium hydroxide, NaOH	. 75 gm./l.
Glucose	. 60 gm./l.

The reaction which takes place on making the solution is as follows:



The bath is operated hot (at about 120° F.) with current densities of the order of 10 amps. per sq. ft.

The solution is not a very satisfactory one from the plating point of view, being unstable and having a very narrow operating range. The stannite tends to oxidise to stannate with the deposition of tin

in a spongy form, resulting in dark, porous deposits. For this reason it has been almost entirely replaced by the stannate bath and the acid solution.

The Stannate Bath.—The stannate bath consists of a solution of sodium stannate with a certain amount of free caustic soda.

A satisfactory bath can be made up from:

Sodium stannate, $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$.	80 gm./l.
Caustic soda, NaOH (free) . . .	12 gm./l.
Sodium acetate	15 gm./l.

In the early stages of its development the stannate bath was uncertain in its operation due to a tendency towards the formation of dark, spongy deposits. Precipitation of tin salts at the bottom of the bath in the form of insoluble sludges was also liable to occur. This condition was eventually found to be due to the development of stannite in the bath. Stannite formation can be prevented by commencing deposition with a relatively high anode current density, until a characteristic yellow-green film forms on the anodes, which shows that the tin is all going into solution in the form of stannate; a dull grey appearance indicates that the tin is dissolving as stannite. Hard water should not be used for making up the bath, as this can also result in the precipitation of insoluble tin salts.

Anodes.—This anode film is maintained as long as the anode current density is high enough and the free caustic soda content is not excessive. The film forms at current densities of as low as 5 amps. per sq. ft. with a low caustic soda content in the solution, but with high caustic soda concentrations greater initial current densities are required. There appears to be a critical anode current density for each solution, below which the tin dissolves in the form of the undesirable stannite, and above which it dissolves as stannate. This current density varies with the caustic soda content of the solution and with its temperature. It also tends to increase with increasing concentration of stannate. If the anode current density becomes too high, on the other hand, the anodes develop passivity and may become coated with an insoluble and tenacious black oxide film.

Good anode connections are essential, as even a few anodes operating under incorrect conditions due to faulty contact may result in the development of sufficient stannite in the solution to cause dark, spongy deposits. Should this occur, the addition of a small amount of hydrogen peroxide (about 0.5 gm. per litre) to oxidise the

stannite is recommended. The anode area should be slightly greater than the mean cathode area passing through the bath.

Caustic Soda Content. The caustic soda content of the bath must be controlled, since if it is allowed to fall too low some of the tin will precipitate out in the form of insoluble hydroxide. Too low a concentration of free caustic soda will also lead to low anode efficiency, although the cathode efficiency may be increased. The carbon dioxide of the air interacts with the caustic alkali to form carbonate, and if this accumulates in excessive amount in the solution it may be necessary to remove some of it, either by freezing out, or by discarding a proportion of the solution.

High concentrations of sodium carbonate result in reduced cathode efficiency, but a small concentration (about 2 oz. per gallon) has a favourable influence.

The effect of solution compositions in relation to operating conditions is shown in Table XXXVI, which is based on data obtained by the Tin Research Council.⁽²⁾

TABLE XXXVI
OPERATING CONDITIONS OF STANNATE PLATING SOLUTIONS

Solution composition (gm./l.)			Cathode current density amps./ sq. ft.	Cathode efficiency	Tempera- ture	Time to plate 0.001 in.
Tin	Na ₂ SnO ₃ , 3H ₂ O	Free NaOH				
						<i>min.</i>
60	135	15	20	82%	73°C.	56
50	112	15	15	85%	72°C.	73
40	90	12.5	15	85%	77°C.	73
30	67	10	10	87%	72°C.	103
20	45	10	10	87%	78°C.	103

Operation of the Bath. The stannate bath has an increasingly low cathode efficiency as the current density increases above about 20 amps. per sq. ft. which limits its application where high-speed plating is concerned. High operating temperatures are desirable, and the solution is commonly maintained at 150° F. to 180° F. The throwing power of the solution is excellent, especially if a high metal concentration is maintained; increased free caustic soda and carbonate also favour good throwing power, while the addition of a small amount of sodium acetate is useful in this direction.

In order to minimise the evolution of unpleasant caustic alkali spray into the atmosphere during the working of the bath, a small proportion of sodium oleate is often added. This addition results in the formation of a protective blanket of foam on the surface of the bath. The presence of metallic impurities, such as lead, arsenic, and antimony in the solution results in dark deposits; impurities may be introduced by the use of poor-quality anodes or salts, but normally they will tend to plate out in due course.

The Potassium Stannate Bath.—More recently, the potassium stannate bath has been experimented with as providing a bath with better plating characteristics than the sodium stannate solution.⁽³⁾ The advantages of potassium stannate are that the use of equivalent stoichiometric quantities of the latter salt increases the bath conductivity very considerably and raises the cathode efficiency, whilst the tendency for sludge formation is reduced. The high solubility of the salt is also an advantage, as is the fact that the solubility increases with temperature, and not the reverse, as is the case with sodium stannate.

A solution containing 190 to 200 gm. l. of tin and 100 gm. l. of free caustic potash operates with a cathode efficiency of 82 per cent at a current density of 150 amps. per sq. ft. and a temperature of 90°C. The corresponding anode efficiency is 84 per cent. With a tin concentration of 140 gm. l. and a free caustic potash content of 115 gm. l., the anode and cathode efficiencies are both 70 per cent, at the same temperature and current density. Increase in the free alkali content of the bath markedly improves the conductivity of the solution, but generally tends to decrease the cathode efficiency. On the other hand, the anode efficiency and the critical anode current density are raised. Increasing the tin content of the bath slightly decreases the conductivity. Fig. 113 shows the comparative efficiencies of equivalent potash and soda baths containing 83 gm. l. of tin and 28 gm. l. of NaOH or 38 gm. l. of KOH.⁽⁴⁾ The anode efficiency in this type of bath at high current densities is said to be improved by the use of an anode containing 1 per cent of aluminium.

The Acid Tin Bath.—The acid tin bath, as used to-day, consists of a solution of stannous sulphate and sulphuric acid, together with various addition agents. The latter are essential since without them the deposits produced are crystalline and non-coherent. Acid tin chloride, fluoride, perchlorate, and fluosilicate baths have been suggested at various times for acid tin-plating, but they have largely been displaced by the acid tin sulphate bath. One alternative acid

bath is, however, worthy of mention since it appears to have had some application in the U.S.A. for the continuous high-speed electro-tinning of steel strip, viz. the stannous fluoborate solution.⁽⁵⁾ A preferred solution consists of:

Fluoboric acid	50 gm./l.
Stannous fluoborate (as tin)	35 gm./l.
Alolin	1 gm./l.

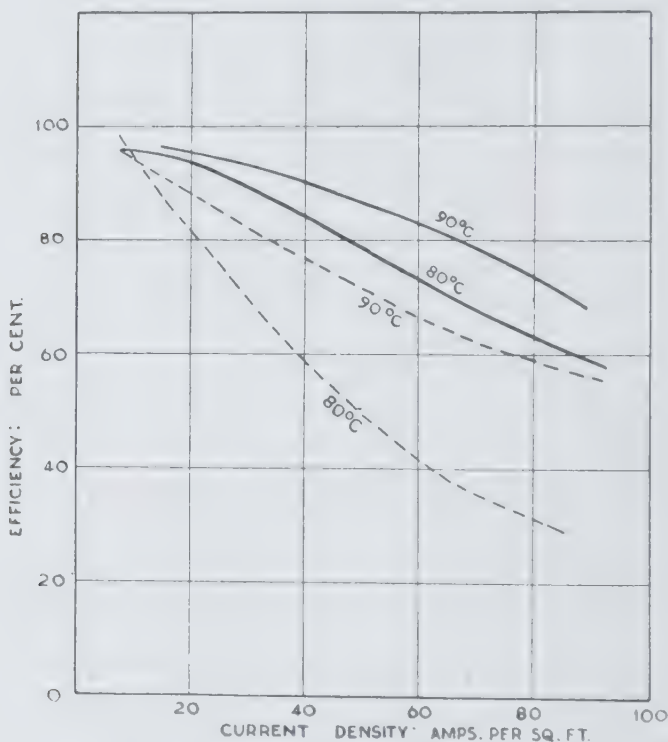


Fig. 113.—Comparative efficiencies of equivalent potash and soda tin-plating baths

Potassium stannate bath ————— Sodium stannate bath - - - - -

Smooth deposits are said to be obtained at current densities of 150 to 300 amps. per sq. ft. at temperatures of 120° F., and with linear strip speeds of 200 ft. per minute through the bath. The solution is claimed to be exceptionally stable, with no tendency to oxidation or to precipitation of the addition agent on standing.

The bath is also applicable to the deposition of lead-tin alloys by first electrolysing with lead anodes until a lead content of 17 gm. per litre has been built up in the solution.

Acid Tin Sulphate Bath.—The addition agents most commonly

employed in conjunction with the acid tin sulphate solution are mixtures of a colloid together with an aromatic compound. A bath which has been widely employed in this country contains gelatine, beta-naphthol, and cresol sulphonie acid as addition agents.⁽⁶⁾ The gelatine acts as a protective colloid since beta-naphthol is practically insoluble in the solution in its absence. The bath contains:

Stannous sulphate	55 gm./l.
Cresol sulphonie acid	100 gm./l.
Free sulphuric acid	60 gm./l.
Gelatine	2 gm./l.
Beta-naphthol	1 gm./l.

The solution can be made up either by dissolving stannous sulphate in the mixed sulphuric and cresol sulphonie acids, or by effecting the anodic dissolution of metallic tin in the acid mixture. The cathodes used are steel plates suspended in porous pots which are filled with dilute sulphuric acid and hung in the bath: 13.5 ampere-hours are required for each gallon of solution to obtain a tin concentration of 30 gm. per litre in the bath. The gelatine is separately dissolved in hot water and the beta-naphthol dissolved in alcohol is added to it slowly, with vigorous stirring. After standing and decanting off any precipitate, the mixture is ready for incorporating in the solution.

The cresol sulphonie acid can be prepared by heating one part by weight of cresol with two parts by weight of concentrated sulphuric acid, for two hours at 110° C. Only about half the sulphuric acid reacts, the rest being left in the resulting product, and this must be taken into account in making up the bath. The presence of cresol sulphonie acid appears to have some value in reducing the tendency for oxidation of the stannous sulphate to occur. Resorcinol has also been employed in acid tin solutions in place of cresol. A recent patent for the tin-plating of strip recommends the addition of cresylic acid and quinol, together with a sulphonated alcohol.⁽⁷⁾

Operating Conditions.—The acid tin solution must be operated in a lead-lined or rubber-lined tank; alternatively, stoneware or acid-resisting plastic tanks can be employed. Room temperatures are generally used, although the optimum working range is at about 70° F. to 80° F.; excessively high temperatures are to be avoided, as they tend to cause oxidation of the solution. The current density should not normally exceed about 10 amps. per sq. ft. unless cathode rod agitation is used; air agitation of the solution is not recommended. In some American plants for the continuous plating of steel strip,

the rapid cathode movement employed enables current densities of up to 400 amps. per sq. ft. to be used without any tendency for burning to occur.

The conductivity of the acid tin solution is high, so that only low operating voltages (about 1 to $1\frac{1}{2}$ volts) are required; the throwing power, on the other hand, is not as good as that of the stannate bath. The "covering power" of the solution depends largely on the addition agents, and if the concentration of these is allowed to fall too low poor crystalline deposits are formed with bare areas particularly at low current density regions. Cathode efficiency is very high, being almost 100 per cent. The anode current density is not critical, but should not exceed about 20 amps. per sq. ft. Pure tin anodes are used.

The solution does not require a high degree of filtration, but excessive amounts of sludge should not be allowed to accumulate as they may cause porosity in the deposits. The acid tin solution is liable to develop sludge owing to oxidation of the tin to insoluble basic compounds and to gradual precipitation of addition agents. Periodic filtration through kieselguhr is helpful in eliminating sludges. (See p. 242.)

Bright Tin.—Deposits from the acid bath are, like those from the alkaline solution, matt in appearance. Bright tin solutions have been patented, however, but have not received wide application; Schlötter⁽⁸⁾ recommends a bright acid bath consisting of:

Tin benzene disulphonate	25 gm./l.
Naphthalene disulphonic acid	115 gm./l.
Glue	1 gm./l.
Benzoin resin	0.8 gm./l.
Alcohol	3 c.c./l.

The tin should not be used in the form of a simple salt as inorganic anions are undesirable in the solution.

Continuous Electro-tinning of Steel Strip.—Many plants have been designed for the continuous electro-tinning of steel strip. The process was originally introduced as a measure of war-time economy to conserve tin, since it is possible to produce tin coatings by this method which are only one-third as thick as the thinnest coatings obtainable by hot-dipping. It was found, however, that the advantages of high-speed plating, the ready control of the thickness of the deposit and its uniformity, coupled with the fact that the steel can be handled continuously in coil form, presented so many advantages that the process will almost certainly become an established

method of making tinplate. A recent plant developed in the U.S.A. has been described by Erbe⁽⁹⁾ which operates at a maximum speed of 1,300 ft. per minute.

The steel strip arrives in the form of coils, about $5\frac{1}{2}$ ft. in diameter, the material being 0.005 in. to 0.015 in. thick and up to 36 in. in width. Such coils contain about three miles of strip and may weigh 12 to 15 tons each. At the entry end of the line the strip is uncoiled and passes through a welding unit which serves to weld the end of each roll on to the beginning of the next. Pinch rolls then transfer the coils through the plating tanks, after which the coating is "re-flowed" by induction heating, quenched, and re-coiled. Both acid and alkaline solutions have been employed in plants of this type, the pre-cleaning cycles being modified according to the type of solution used. In general, the acid solutions require a rather more efficient cleaning cycle than the alkaline baths, which have detergent properties. A variable speed horizontal tank plating line, including tinning, re-flowing, and cutting into sheets, is shown schematically in Fig. 114. Fig. 115 shows the delivery end of a typical continuous electro-tinning unit for steel strip.

A recent installation for the continuous electro-tinning of steel strip operating in Great Britain has been described by Frenkel.⁽¹⁰⁾ The strip travels through deep plating tanks in a vertical plane at speeds of about 1,000 ft. per minute. Pre-cleaning is carried out in an alkaline cleaner followed by pickling in weak sulphuric acid, spray rinsing and scouring with fibre brushes. It is then ready to enter the acid-type electrolyte, where plating is carried out at up to 200 amps. per sq. ft. The tin anodes are suspended vertically on both sides of the strip and are about 5 ft. long. They are inserted

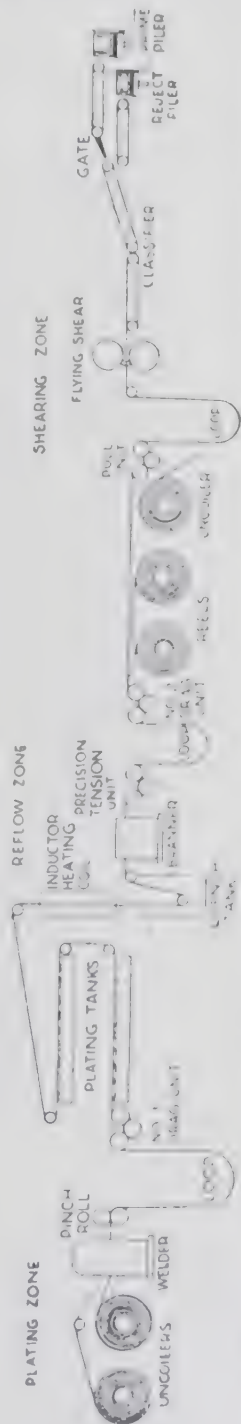


Fig. 114. A variable-speed, horizontal tank strip-plating line, including tinning, reflowing and cutting into sheets.

new at one side of the tank, whilst the worn ones are removed at the other; in this way they travel horizontally across the face of the strip which is moving vertically. Provision is made for the additional thickness of the new anodes as compared with the worn ones to ensure that the anode-cathode distance is kept constant.

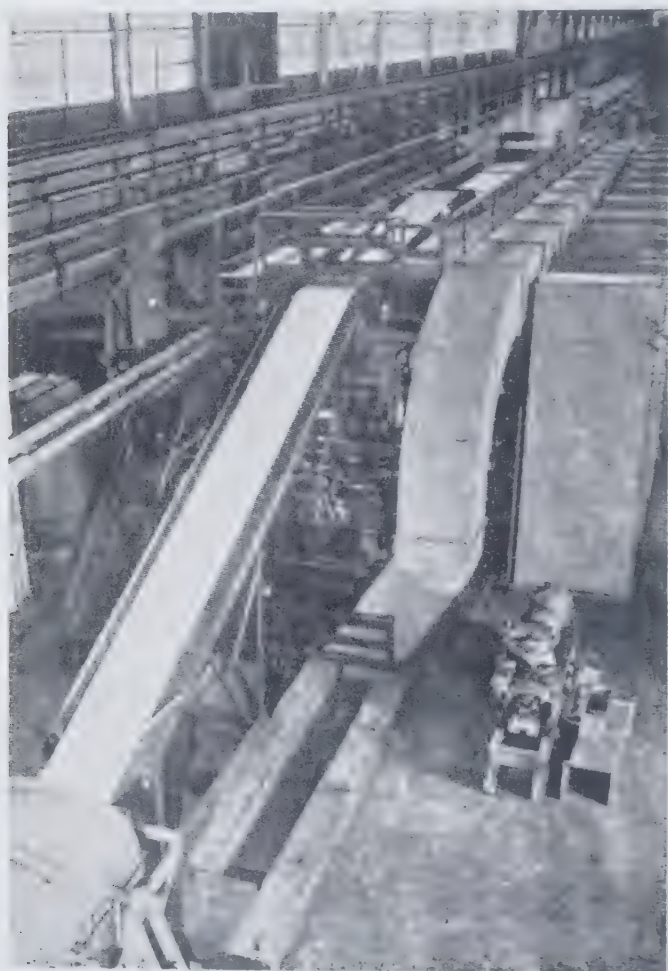


Fig. 115.—Electrolytic tinplate emerging from the after-plating rinse at 1,000 ft. per min.

The current is conveyed to the strip through five water-cooled conductor rolls. The anode efficiency of the plant is practically 100 per cent, the cathode efficiency being seldom less than 95 per cent.

There is naturally a high drag-out rate, and the tin from this is recovered electrolytically. The matt tinplate as it emerges is

"reflowed" by resistance heating to produce a bright finish as described below.

Re-flowing Procedure.—The tinned sheet as it emerges from the bath has the characteristic matt surface of the electro-deposited metal. This finish is not acceptable to the tinplate trade, so that it is the usual practice to "re-flow" the deposit by momentarily melting the coating by suitable means. In this way, the typical bright finish of commercial tinplate is obtained.

Re-flowing can be accomplished either by passing the strip through a hot oil bath, through a suitable furnace to heat the tin to its melting-point (450°F.) or by the use of high frequency induction heating.

Palm oil is usually used for hot oil re-flowing, but as the temperature of the oil cannot be raised much above the melting-point of the tin without decomposition, the rate at which the strip can pass through such a bath is strictly limited. Heating by radiant furnaces suffers from the same limitations, since up to 6 in. of furnace length must be allowed for each foot per minute at which the strip travels. This means that if the speed of the furnace conveyor is in excess of 200 to 300 ft. per minute, the use of furnace re-flowing becomes impracticable. Neither this method nor the hot oil process lend themselves to incorporation in the electro-tinning line where large outputs are required.

High frequency induction heating is a very satisfactory method of re-flowing, since by this means rapid heating is obtained without the need for contact being made with the strip.

For induction heating an oscillator of about 100 to 200 kW. capacity is necessary where a strip speed of 1,000 ft. per minute is to be dealt with. The heating zone need only be about 10 to 12 ft. in length.

Electric resistance heating is, however, a cheaper and entirely simple manner of re-flowing the tin, provided careful precautions are taken to prevent damage at the contacts between the current-carrying rolls and the strip. Should arcing take place, the plate will be damaged locally. Spring-loaded rollers operating under water have been successfully employed for this purpose and have given little trouble.

After re-flowing the tinplate is passed through a weak chromic acid solution to eliminate the staining and darkening of the sheet which occurs in lacquering or printing unless this is carried out. Such discoloration is due to the porosity of the thin coat which exposes the lacquer to the underlying steel. The passivating effect of the chromic acid eliminates this.

As a final operation the strip is passed through a hot emulsion of cotton-seed oil which serves as a lubricant and a protective in storage. It is then cut up by a rotary flying shear into sheets which are automatically sorted into primes and rejects by electronic pin-hole detectors and a flying micrometer.

Relative Merits of Hot-dip and Electro-tinning.—Hot-dipped tin coatings of a thickness of less than $1\frac{1}{4}$ lb. per base-box cannot readily be produced. (The term "base-box" is one used in the tinplate industry to denote 112 sheets of tin or terne plate, each having an area of 14 in. by 20 in., corresponding with a total surface area of 217.78 sq. ft.) The usual standard thickness is, however, about $1\frac{1}{2}$ lb. per base-box, corresponding to a thickness of about 0.00012 in. of tin. With the introduction of electro-tinning it was found practicable to produce coatings of only about $\frac{1}{2}$ lb. per base-box (0.00003 in. to 0.00004 in. thickness) and sheet of this type has been produced in considerable quantities, particularly in the U.S.A. More recently, however, it has become increasingly evident that tin coatings as thin as this are inadequate for their purpose, particularly in the canning industry, and a minimum thickness of about 1 lb. per base-box is probably essential for the production of satisfactory tinplate.

Protective Film on Tinplate.—A "passivating" treatment for tinplate which effectively reduces the tendency for corrosion to occur at regions of local porosity and also reduces liability of the plate to sulphur blackening when certain vegetables are canned, has recently been introduced.⁽¹¹⁾ It consists in immersing the plate for five minutes in a solution of:

Trisodium phosphate cryst.	. 40 gm./l.
Sodium hexametaphosphate	. 20 gm./l.
Sodium dichromate . . .	. 12.5 gm./l.
Sodium hydroxide . . .	. 14 gm./l.
Perminal KB	. 5 c.c./l.

The temperature of the solution is kept at 85° C. to 90° C. and the pH is controlled at 12.5.

The treatment appears to be very effective.

SPECULUM ALLOY

During recent years a co-deposit of copper and tin has been introduced under the name of speculum alloy for articles of jewellery, tableware, bathroom fittings, and the like. The preferred composition

of the alloy is 45 per cent tin and 55 per cent copper, this being similar to the composition of the ancient speculum mirrors produced by the Romans 2,000 years ago. These mirrors were produced by casting, owing to the brittle nature of the metal.

Speculum alloy has a pleasing appearance, being whiter than chromium, is resistant to washing, and has good wearing properties. It does not tarnish easily in indoor atmospheres, and is not attacked by most foods, including those which contain sulphur, such as eggs. The protective value of the deposit against severe atmospheric corrosion is not high, however, and speculum-plating is not recommended for outdoor service. The deposit is also liable to be porous, but this tendency can be reduced by regular filtration of the plating solution.

The tarnish resistance of speculum deposits has resulted in some attention being given to their possibilities in the manufacture of reflectors. The reflectivity of speculum is about 65 per cent, and for some types of reflector under suitable conditions it would give satisfactory service. Where the reflector is liable to become excessively heated, however, speculum develops a milky film, and although this can be readily cleaned off, the reflectivity of the surface is greatly lowered by its presence. For this reason speculum deposits should not be exposed to temperatures in excess of 100°C. to 120°C. if their reflectivity is to be maintained.

The most serviceable range of deposits contains from 39 to 55 per cent of tin. Within these limits, tin-copper alloys in equilibrium consist of inter-metallic compounds, and it is to these that the hardness and tarnish resistance of the speculum is probably due. With tin contents of less than 39 per cent the deposit lacks resistance to tarnish, whilst if the tin is higher than 55 per cent the coating is soft.⁽¹²⁾ The solution used for speculum-plating consists of an alkaline sodium stannate bath containing copper cyanide. The solution is operated in an iron tank, a suitable composition being:

Sodium stannate, $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$	90 gm./l.
Copper cyanide, CuCN	11 gm./l.
Sodium cyanide (free)	16 gm./l.
Sodium hydroxide (free)	15 gm./l.

Glass linings are undesirable as they tend to be attacked by the solution.

Anodes.—In operating the bath separate tin and copper anodes are employed, using individual circuits for each type of anode. Thus, the current density at the copper and at the tin anodes can

be separately controlled by means of a resistance board in each circuit.

Pure tin anodes are employed, and must be kept filmed, as is the usual practice in tinplating from the stannate solution. (See p. 365.) The anode current density should not fall below 12 amps. per sq. ft. or the film will be lost and stannite will form in the bath. The result will be dark, rough and brittle deposits. For this reason the tin anodes should be lifted from the bath when the solution is not in use. If stannite should form it can be oxidised to the stannate by the addition of small quantities of sodium peroxide.

The copper anodes are preferably of the flat electrolytic type; the current density should be about 10 amps. per sq. ft.

Working Conditions.—A suitable solution from which speculum alloy can be satisfactorily plated has been given above. The free caustic soda content should be about 15 gm. l. Investigations have shown that low concentrations of hydroxide increase the amount of tin in the deposit and the cathode efficiency, and vice versa. This effect enables the sodium hydroxide content to be employed as a means of controlling the composition of the deposit.

Similar considerations apply to free cyanide, and these two variables must be closely controlled for successful results.

The working temperature is about 65 C.; the cathode efficiency increases almost linearly with temperature, but temperatures above 65 C. are undesirable, as they cause excessively rapid carbonate formation and cyanide decomposition. Increasing current density results in a marked reduction in cathode efficiency; current densities should not exceed about 25 amps. per sq. ft. The effect of current density on the composition of the alloy is surprisingly small.

Speculum alloy, as deposited, is slightly milky in appearance, but is readily buffed to a high lustre. Faulty deposits can be rectified by re-plating without stripping.

Speculum alloy is not a suitable undercoat for chromium, as satisfactory deposits of the latter metal cannot readily be applied to it.

TIN-ZINC ALLOYS

Co-deposits of tin and zinc have been the subject of recent investigations, and a highly corrosion-resisting alloy containing 7.8 per cent of tin and 22 per cent of zinc has been described by Angles.⁽¹³⁾

The electrolyte employed for plating the alloy contains sodium stannate and zinc cyanide, the ratio of tin to zinc being maintained at 12 : 1 approximately. A recommended solution consists of:

Tin (as sodium stannate, $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$)	30 gm. l.
Zinc (as zinc cyanide, $\text{Zn}(\text{CN})_2$)	2.5 gm./l.
Sodium cyanide (total)	25 gm./l.
Sodium hydroxide (free)	4 to 6 gm. l.
Temperature	70°C.
Cathode current density	10 to 40 amps. sq. ft.
Anode current density	7.5 to 15 amps./sq. ft.

The anodes may be rolled or cast, and must be kept in the filmed condition, as in tin-plating from the stannate bath to ensure that no stannite forms in the solution. (See p. 365.)

By altering the tin zinc ratio in the solution it is possible to alter the composition of the alloy. Thus a 50 : 50 zinc-tin alloy can be deposited using anodes of the same composition. The zinc content of the bath should, however, be raised to about 8 gm. l. whilst the sodium hydroxide content should be about 6 to 8 gm. l. with 50 gm. l. of sodium cyanide at a current density of 15 amps. per sq. ft. These solutions will deposit about 0.0005 in. of alloy in half an hour and this thickness affords adequate protection for most purposes.

The conditions of operation of the bath are not critical, cleaning before plating being similar to that which is usual prior to ordinary zinc-plating. In certain cases where blistering is prone to occur (as with soft solder, for example) scouring with pumice or a copper flash may be necessary before immersion in the alloy plating bath.

The high-tin alloy (80 : 20) has been successfully employed on radio chassis, being outstandingly resistant to tropical conditions and readily solderable. The 50 : 50 alloy is also easily solderable and gives a greater degree of sacrificial protection should the plate be damaged. Under normal conditions, however, the alloys with the higher tin content are more protective. The coatings are very flexible and the plated metal is able to withstand a greater amount of deformation without the corrosion-resistance of the coating being reduced than is the case with either tin or cadmium.

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CADMIUM, ZINC, AND LEAD PLATING

CADMIUM-PLATING

Cadmium-plating has found considerable application in recent years primarily for the protection of ferrous metals against corrosion. The metal is more attractive in appearance than zinc when electro-deposited, being whiter and more lustrous. It is, however, much more expensive than the latter metal, and this has, to some extent, limited its general application.

Relatively thin deposits of cadmium on steel effectively protect parts under reasonable conditions of exposure, and for this reason the finish is widely employed on light equipment, such as radio chassis, motor-car electrical equipment, refrigerator and vacuum cleaner components, and numerous small accessories, such as screws, nuts, etc. Cadmium also has the great advantage of being much easier to solder on to than zinc, while its greater resistance to alkalis makes it useful in domestic equipment. The resistance to acids is low, however, and cadmium-plating should not be used on parts that are likely to come into contact with foodstuffs (especially those of an acid nature) because of the toxicity of cadmium and its compounds.

Cadmium is sometimes plated on to brass and copper alloy parts, especially for military purposes. Its protective value on these metals is not high, except possibly where brazed assemblies incorporating steel parts are concerned; here the cadmium may serve to reduce the tendency for electro-chemical corrosion to occur at the junction between the two metals.

For outdoor exposure heavier deposits of cadmium are extensively used on steel components, especially on aircraft and marine equipment, because of the good protection such deposits give under these conditions. Typical examples are seen in Fig. 116, which illustrates an aircraft engine bearer, and in Fig. 117, which shows various other aero-engine components. Where high humidity conditions prevail, the cadmium protects the underlying ferrous metal anodically, so that preferential corrosion of the cadmium takes place before the underlying steel is attacked. Corrosion products of the coating metal are also less likely to form on cadmium under adverse conditions than on zinc.

The Plating Solution.—Cadmium is almost exclusively deposited from the cyanide solution, because of its good "throwing power" and the fine-grained smooth deposits obtained. Acid sulphate electrolytes have been employed for the electro-refining of the metal, but the deposit is rough and nodular (unless some organic addition agent is present), so that the solution has found practically no use in electro-plating.

The cyanide bath may be made up by dissolving either cadmium

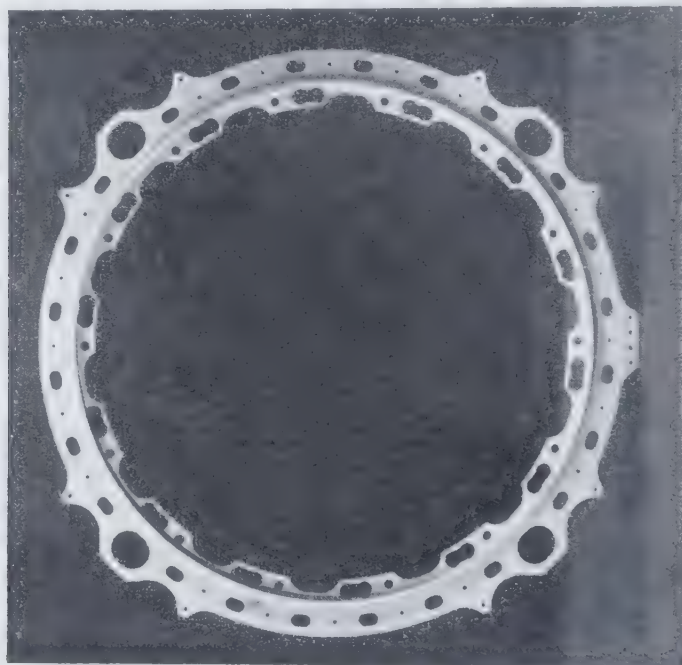
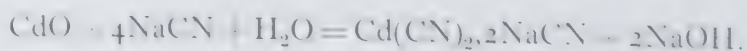


Fig. 116.—Cadmium-plated aircraft engine bearer

oxide or cadmium cyanide in a solution of sodium cyanide. A suitable bath for general work can be made from:

Cadmium cyanide, $\text{Cd}(\text{CN})_2$	. 6 oz.
Sodium cyanide, NaCN	. 8 oz.
Water	. 1 gallon

If cadmium oxide, CdO , be employed, additional cyanide is required to convert the oxide to cyanide in accordance with the equation:



The excess sodium cyanide above that required for the formation of the compound $\text{Cd}(\text{CN})_2 \cdot 2\text{NaCN}$ may be regarded as the "free"

cyanide content of the solution.⁽¹⁾ Thus, each 1 lb. of cadmium oxide requires 1.53 lb. of sodium cyanide to form the double cyanide whilst 1 lb. of cadmium cyanide only requires 0.46 lb. of sodium cyanide. When cadmium oxide is used, a certain amount of sodium hydroxide is left in the solution, but with cadmium cyanide no caustic soda is initially formed unless it is introduced separately.

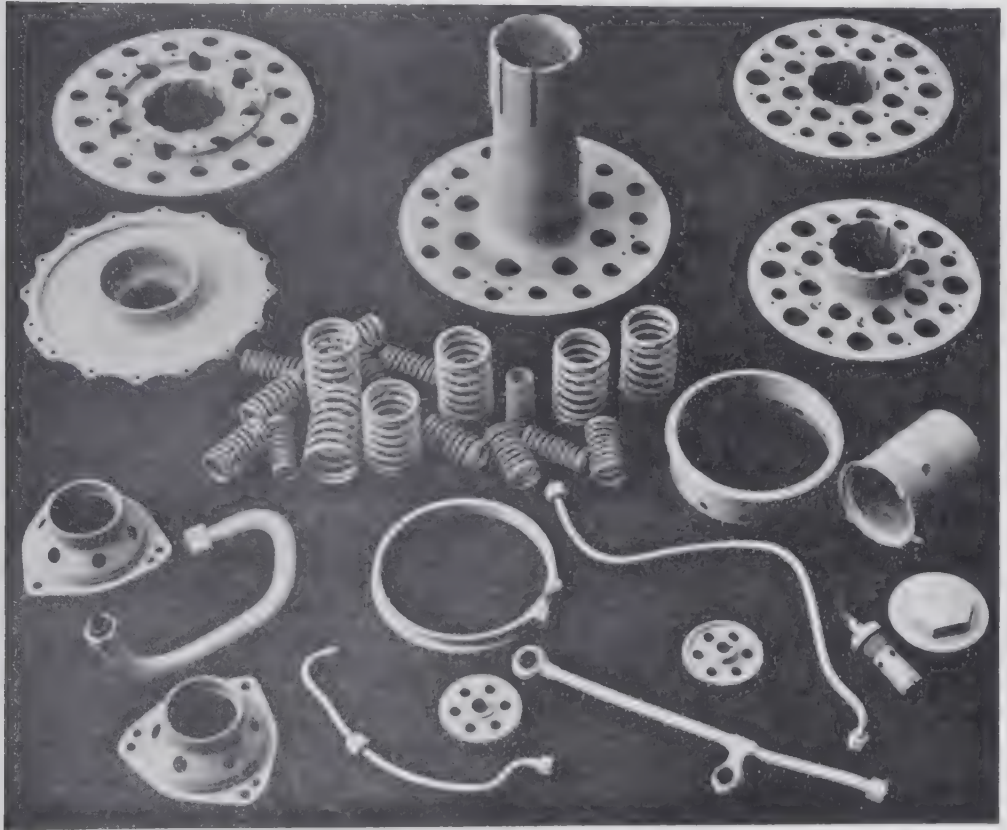


Fig. 117.—Some typical cadmium-plated aero-engine components

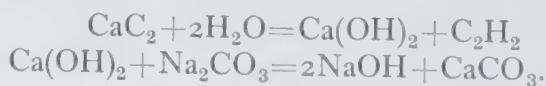
The “free” cyanide content employed can vary widely in cadmium-plating solutions. In view of the variations in the metal content of different baths, the solution can be more satisfactorily controlled by maintaining a suitable ratio between the total cyanide and the metal content; a ratio of $3\frac{1}{2}$ or 4 to 1 is a suitable operating range for most purposes. Sufficient “free” cyanide must be present to maintain anode corrosion, but excessive amounts reduce the cathode efficiency of the solutions rapidly. Concurrently with this reduction in efficiency, however, high free cyanide gives improved “throwing power”, but excessive amounts tend to cause the deposit to become spongy.

The pH control of cyanide solutions is also of value and is increasingly being used. The best pH range, particularly from the point of view of adhesion of the deposit, is 12.0 to 13.0.⁽²⁾

The metal content adopted depends on several factors. With increased cadmium concentrations (up to 6 oz. per gallon of metal) it is possible to plate with higher current densities, but at the same time, the "throwing power" of the solution is reduced and the deposit may become rough and nodular; also the drag-out losses are higher, which is an important consideration in the case of relatively expensive solutions.

Caustic soda is not an important constituent of the bath, although a small amount improves the conductivity of the solution; it is therefore useful in barrel-plating. As has already been stated, a certain amount of caustic soda is formed when the bath is made up by dissolving cadmium oxide in the cyanide; it is not usual, however, to add caustic soda, as is the case with zinc solutions, because the advantages are not so marked, although a small concentration increases the cathode efficiency somewhat. Sodium carbonate gradually accumulates in cadmium solutions owing to decomposition of the cyanide by the action of the carbon dioxide of the atmosphere. Excessive concentrations of carbonate impair the efficiency of the bath; generally, amounts in excess of 6 to 8 oz. per gallon should not be allowed to accumulate. The sodium carbonate can be removed by crystallising it out by cooling to 0° C., or more easily by discarding a portion of the solution.

A more recent method for the removal of excess carbonates from plating baths consists in treating the solution with calcium carbide, whereby the carbonate is precipitated as calcium carbonate with the liberation of acetylene. (See p. 346.)



This is better than freezing, which only operates successfully when the carbonate concentration is in excess of 10 to 12 oz. gall. Owing to the liberation of 1 oz. gall. of caustic soda by every 0.8 oz. gall. of calcium carbide added, the treatment should be carried out gradually to avoid excessive concentrations of free caustic soda.

Cadmium-plating Practice.—Cadmium-plating solutions are usually operated in steel tanks at room temperature and the current density range under commercial conditions is most generally of the order of 10 to 30 amps. per sq. ft. For the higher current densities, solutions with a greater metal content are necessary (up to 6 oz.

per gallon of cadmium). The cathode efficiency of a cadmium solution is generally reasonably high, i.e. about 85 to 95 per cent, or even more.

Amongst the troubles that can occur in cadmium plating practice are:

- (a) *Burnt deposits.*—This is often the result of too low a metal content in the solution, provided the bath is being worked at the correct current density.
- (b) *Dull deposits.*—This condition can result from the solution being out of balance, viz. too high in caustic or carbonate content, or too little free cyanide. Excessively high metal content can have a similar effect.
- (c) *Pitting of the deposit.*—This is sometimes caused by too little caustic soda in the solution and can be corrected by the addition of a small amount. More often, however, pitting is due to inadequate cleaning or pickling.

Effect of Impurities.—Cadmium-plating is normally of an attractive white colour, but the deposit is susceptible to discoloration if impurities be present in the solution, particularly lead, arsenic, thallium, antimony, tin, and silver.⁽³⁾ The heavy metals can cause trouble when present in amounts exceeding about 0.05 gm. per litre, leading to dark, coarse, and spongy deposits; arsenic is the worst offender and amounts as low as 0.005 gm. per litre can have a marked detrimental influence.⁽⁴⁾ Thallium also occasionally causes trouble, being introduced from anode sludges. Should these impurities be introduced from anode sludge or by other means they can be removed either by prolonged electrolysis at current densities of 1 to 3 amps. per sq. ft., or by displacement by means of cadmium dust, followed by filtration of the solution. Nitrates are also to be avoided in cadmium solutions, as they markedly lower the cathode efficiency of the bath; sulphates have little adverse influence.

Nickel has a brightening influence in cadmium solutions when present to the extent of about 0.2 to 0.3 gm. per litre.

Addition Agents.—Brighteners and addition agents are also added to cadmium-plating solutions to some extent, including nickel and cobalt salts of aryl sulphonic acids, starch, dextrose, etc., and numbers of them have been patented. Certain addition agents facilitate plating at higher current densities, but their concentration must be kept low or the efficiency of the solution will be reduced.

Anodes.—The anodes are usually cast and should be as pure as possible, while the anode current density should not exceed about

15 to 20 amps. per sq. ft. if uniform anode dissolution is to be obtained. On the other hand, excessively low current densities are also undesirable as they may cause sludging to occur at the anodes.

Cadmium anodes dissolve chemically in the plating solution resulting in high anode efficiencies which may exceed 100 per cent. The rate of solution increases with rising temperature and cyanide content of the electrolyte. An anode/cathode ratio of about 1 : 3 is therefore best maintained if excessive metal dissolution is to be avoided, additional anode area being provided by the use of steel anodes, if necessary.

The presence of even small impurities in cadmium anodes is harmful. Lead, silver, tin, thallium, arsenic and antimony cause dark, coarse deposits. As little as 0.01 oz. per gallon of antimony and one-tenth of this proportion of arsenic have been stated to result in dark, rough or spongy deposits, although these metals are not deposited at the cathode.

The anodes used may be of the oval type with cast-in hooks, or cadmium balls can be used in steel cages (Fig. 118). The latter arrangement has the advantage that additional balls can be added to the top of the cage as dissolution takes place, and ensures that an adequate anode surface is present towards the bottom of the plating tank. It has the disadvantage, however, that poor contact between the balls and the cage can result under certain conditions. Cadmium anode balls in steel cages are not subject to complete polarisation under any current density conditions, however, owing to the high oxygen over-voltage on steel as compared with the over-voltage on cadmium. This means that the cadmium anode does not become inactive while the steel surface is active. It is noteworthy, in this connection, that



Fig. 118. — Cadmium ball anodes in steel wire cage

if inert steel anodes are used alone (e.g. for the reduction of the metal content of the solution), they tend to become coated with an oxide deposit and must be cleaned from time to time if a reasonable working voltage is to be maintained.

A novel type of anode which has been employed with some success



Fig. 119.—Fully immersed plating barrel

in this country is the “gear” anode in which oval gear-shaped sections are threaded over a central support. These sections can be turned about their axis to facilitate the plating of articles of awkward shape, while the toothed surface is said to result in more uniform wear than is the case with oval or rolled sheet anodes.

When the anodes are working correctly their appearance is dull grey, but with excessive anode current densities a black coating may form on their surface. Further increase in current density results

in white salt deposits on the anodes accompanied by considerable oxygen evolution. An increase in the "free" cyanide tends to increase the permissible maximum anode current while high concentrations of sodium carbonate tend to act in the reverse direction in most types of solution.

Generally speaking, polarisation of the anodes is due to excessively high anode current densities, too high a carbonate content, or too little caustic or cyanide in the solution. Anode polarisation is to be avoided, since it can lead to the formation of rough deposits.

If the bath should become contaminated with metals more noble than cadmium, these may tend to deposit out on the anodes in the form of a slime. Such contaminants can be removed by electrolysis at low current density or by means of cadmium sponge or dust.

Cadmium lends itself to barrel plating for small parts, an excellent finish being generally obtained in a short time. The best type of modern barrel is fully immersed, being made of a suitable plastic such as a methacrylate resin. Fig. 119 shows a barrel of this description. The internal contacts to the work are carried on flexible rubber-covered arms, thus facilitating good electrical contact with the work in the barrel and at the same time making it a simple matter to renew the contacts if necessary when excessive build-up of metal occurs on them.

After-treatment of Cadmium Deposits.—Cadmium, as deposited, presents an attractive semi-bright appearance, although the actual degree of brightness varies with the nature of the surface of the underlying metal. Sometimes, however, the appearance of cadmium is improved by various bright dips, which consist essentially of solutions of oxidising agents. The cadmium appears to dissolve in these without gas evolution, and a brightening effect is produced by immersion for a few seconds in the solution. The commonest bright dips for cadmium are: (a) chromic acid; (b) peroxide dips; and (c) nitric acid. In the first of these, the plated article is immersed for two or three seconds in a solution of chromic acid containing a small amount of sulphuric acid. A typical solution consists of 250 gm. per litre of chromic acid with about 0.3 to 0.5 gm. per litre of concentrated sulphuric acid. The solution attacks the cadmium fairly rapidly, so that immersion must not be excessively prolonged. The peroxide dip consists of a solution of hydrogen peroxide (5 to 10 per cent by volume of 30 per cent (100 vol.) hydrogen peroxide) and about 0.3 to 0.5 per cent of sulphuric acid. The nitric acid dip is simply a dilute aqueous solution of nitric acid of 0.5 to 1 per cent strength.

The chromic acid dip reduces the intrinsic corrodibility of the cadmium, while both this and the peroxide dip reduce the tendency for the deposit to stain and finger-mark. The nitric acid dip is less valuable from the latter point of view.

The durability of cadmium plate under many conditions can be improved by chromate passivation. (See p. 400.)

ZINC-PLATING

Zinc is deposited from either the cyanide or the sulphate solution. The cyanide bath is the more expensive to operate, but has the advantages of greater "throwing power" and the fact that the solution can be used in steel tanks. Rubber-lined tanks can also be used with advantage, while rubber-covered steel or synthetic resins are employed for barrels.

Zinc deposits are employed on a wide variety of steel components, the metal being much cheaper than cadmium. It is inferior in appearance to the latter metal, although the more recently developed bright zinc solutions have to some extent remedied this deficiency. A more serious disadvantage, however, is the tendency for zinc deposits to corrode in damp atmospheres and to become coated with a white gelatinous deposit. This can be minimised by chromate dipping, however. (See p. 400.) Zinc deposits are generally considered to be slightly superior to cadmium deposits for the protection of steel in industrial atmospheres, but less satisfactory under marine and tropical conditions.

Cleaning before Plating.—The acid zinc bath is superior to the cyanide solution where cast iron or malleable iron have to be plated. The relatively lower "throwing power" of the acid bath and its tendency to produce crystalline deposits can to some extent be reduced by first plating a thin zinc deposit from a cyanide bath, following this by a heavier deposit from the acid solution.

Cleaning prior to plating must be more meticulously carried out in the case of the acid solution than when the alkaline bath is employed, because of the greater detergent action of the latter.

Alkali cleaning, with or without current, followed by pickling in a solution of hydrochloric acid or sulphuric acid are the usual pre-treatments for the zinc plating of steel. Trichlorethylene degreasing or emulsion cleaning are also often used before pickling.

A recommended procedure for the pre-treatment of articles difficult to plate because of the presence of deep recesses is to treat them in a special pickle consisting of a 10 per cent solution by volume of hydrochloric acid to which about 8 oz. per gallon of zinc chloride

has been added; this pickle is used after the normal pickle. After pickling and rinsing, a dip in a cyanide solution is helpful before immersion in the cyanide plating bath. This reduces the tendency for iron salts to accumulate in the plating solution.

Castings, pressings, and stampings can also be barrel-tumbled, shot-blasted and then lightly pickled. Anodic etching in sulphuric acid is also helpful in promoting adhesion on cold-rolled surfaces.

The Cyanide Bath.—The straight cyanide bath consists of a solution of zinc cyanide, together with a certain amount of sodium cyanide and sodium hydroxide. A typical solution consists of:

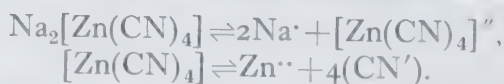
Zinc cyanide, $\text{Zn}(\text{CN})_2$	.	.	9 oz./gall.
Sodium cyanide, NaCN	.	.	8 oz./gall.
Caustic soda, NaOH	.	.	11 oz./gall.

Alternatively, zinc oxide may be used in place of the cyanide in which case additional cyanide is required to form cyanide from the oxide:



The oxide dissolves readily in a warm solution of sodium cyanide. Various addition agents have been added to zinc cyanide baths to improve their "throwing power" and the appearance of the deposit. Molybdenum salts, surface-active agents, gum arabic, and sodium fluoride are materials which have been used with a measure of success.

Chemically, the solution consists of a mixture of the double cyanide of zinc, $\text{Zn}(\text{CN})_2 \cdot 2\text{NaCN}$, and sodium zincate, Na_2ZnO_2 , together with a certain amount of free caustic soda and or free cyanide which are essential for deposition to occur. The exact proportions of the various constituents present in the bath are very difficult to determine. The solution dissociates as follows:



The fact that only a small proportion of the zinc is present as anion due to the low degree of secondary dissociation accounts for the good throwing power of the solution. Zinc-plating solutions can be conveniently controlled by means of the free caustic soda and the total cyanide contents. An alternative, and in many cases a more satisfactory method of control, is by maintaining the ratio of total cyanide to metal concentration, as the optimum cyanide concentration is dependent on the metal content of the solution. A ratio of 2.5:1 is satisfactory for most normal plating conditions.

While the sodium cyanide-zinc cyanide complex always contains a proportion of zincate, even if no sodium hydroxide be added, some further addition of sodium hydroxide is desirable as this helps to increase the efficiency of the solution and improves the appearance of the deposit. To some extent, the hydroxide is slowly converted to carbonate due to the action of atmospheric carbon dioxide, but further formation of caustic soda can occur in the solution if much hydrogen is liberated on account of reduced cathode efficiency.

High metal and caustic soda contents (up to 15 oz. per gallon) have been used to increase the efficiency of the bath, and under such conditions current densities of 60 amps. per sq. ft. or more can be successfully employed. The high caustic soda types of solution have also excellent "throwing power".

The Zincate Bath.—It is also possible to deposit zinc from a solution of sodium zincate without the presence of cyanide, but usually the deposits obtained are of poor appearance.

Tope⁽³⁾, on the other hand, describes a solution consisting essentially of sodium zincate which is buffered with Rochelle salt, and is claimed to give good deposits at current densities of up to 40 amps. per sq. ft.

The solution consists of:

Zinc sulphate	.	.	.	.	37 oz./gall.
Sodium hydroxide	.	.	.	.	28 oz./gall.
Sodium carbonate	.	.	.	.	14 oz./gall.
Sodium sulphate	.	.	.	.	6 oz./gall.
Sodium cyanide	.	.	.	.	4 oz./gall.
Rochelle salt	.	.	.	.	10 oz./gall.

The cyanide reduces anode polarisation and prevents the formation of anode slimes. It also refines the grain of the deposit.

The chief advantage of this type of solution is that it enables deposition to be carried out more rapidly on to shot-blasted surfaces and on to cast iron than is the case with the normal cyanide solution.

Plating Conditions.—Zinc baths are commonly operated in steel tanks at room temperature, but at higher temperatures (of the order of 100° F. to 110° F.) improved current efficiencies of 90 to 95 per cent can be obtained. The baths are normally operated at current densities of 10 to 30 amps. per sq. ft., but considerably higher current densities can be successfully employed by using solutions of higher metal and caustic soda content operated at temperatures of 120° F. to 130° F.

Anodes.—The zinc anodes tend to dissolve in the solution at more than 100 per cent efficiency so that excessive metal concentrations can build up, resulting in a tendency for rough or nodular deposits to occur. Some use has been made of aluminium in the zinc to control the rate of anode dissolution. The aluminium may be alloyed alone with the zinc or mercury may also be added.⁽⁶⁾ Aluminium is said to favour uniform anode corrosion with little sludge formation; the aluminium is not co-deposited with the zinc. More recently magnesium and cadmium have been proposed as alloying constituents of zinc anodes to reduce the rate of dissolution of the zinc.⁽⁷⁾ To some extent a proportion of steel anodes is useful in zinc solutions to prevent excessive build-up of metal. None of these methods, however, reduces the rate of attack during periods when the bath is not in use. This is especially the case when zinc ball anodes are employed in steel cages, which tend to accelerate the rate of attack on the zinc. Hull⁽⁸⁾ has therefore suggested the use of a light gauge steel sheet suspended from the cathode bar when the bath is not in production. The plate should have an area at least one-half that of the zinc anodes and be kept anodic by means of a small battery. It was found that a current of only 0.20 amp. per sq. ft. prevented any zinc from passing into the solution. For most installations a small 2-volt battery will do all that is required, and arrangements can be easily made for switching in the counter-current unit after suspending the steel plate from the cathode bar. The total current for a 1,000-gallon steel tank will be well under 2 amps.

BRIGHT ZINC-PLATING

More recently bright zinc baths have been introduced to give a whiter and more lustrous deposit than the bluish-grey coating normally produced from the usual type of cyanide bath. In this way zinc deposits can be obtained which approach the more attractive, but considerably more expensive, cadmium-plating.

Bright zinc deposits are obtained by the use of various addition agents in the solution and a considerable number of these have been patented.⁽⁹⁾ The compounds used include such diverse materials as piperonal, thiourea-formaldehyde resins, and molybdenum compounds. Molybdenum is, however, perhaps the most important brightener, and is usually added to the solution in the form of molybdic acid, MoO_3 .⁽¹⁰⁾ These addition agents, besides improving the lustre of the deposit, may also increase the throwing and covering power of the solution.

A typical bright solution consists of:

Zinc oxide		7.5 oz./gall.
Sodium cyanide		15.0 oz./gall.
Caustic soda		12.0 oz./gall.
Molybdic acid		0.25 oz./gall.
Urea		1.0 oz./gall.
Sodium thiosulphate		0.5 oz./gall.

The bath is operated at 60 F. to 90 F., and the current density can range from 15 to 40 amps. sq. ft. The solution has good throwing power and covering properties. The sodium cyanide should be between 14 and 20 oz. gall. and the caustic soda between 10 and 16 oz. gall. The sodium cyanide to zinc ratio is kept at 2.6:1 and the caustic soda to zinc at 2.0:1.

For barrel plating, the solution should be rather more concentrated.

Effects of Contaminants.—The chief essential in bright zinc-plating is to maintain a high standard of purity of the solution and anodes since even slight contamination with heavy metals can cause the deposits to become dark in colour and lose their lustrous appearance. Particularly objectionable are traces of lead and to a lesser extent, copper and iron. Concentrations of heavy metals as low as 0.02 per cent are sufficient to affect the appearance of the deposits appreciably.

Chromic acid has a very marked effect if it should find its way into the solution, and as little as 0.01 gm. per litre of chromium will reduce deposition in low current density areas while higher concentrations may prevent deposition entirely.

Heavy metal contamination can be removed by treatment with zinc powder at the rate of 1 lb. per 100 gallons of solution which precipitates out many foreign metal contaminants, or by the addition of a small amount of a solution of sodium sulphide. Sodium hypsulphite is also useful as a purifying agent. In each case the precipitated impurities can be left to settle out, but the most satisfactory procedure is to filter them off.

Control.—According to Hull and Wernlund,⁽¹¹⁾ apart from maintaining the purity of the solution, the most important factor in successful bright zinc-plating is accurate control of the ratio of total sodium cyanide to zinc metal content. For a typical bright zinc solution it was found that this ratio must lie between 2.5 and 2.7 for operation with high current efficiency at normal current densities and at room temperature. With lower ratios the current density range in which bright deposits are obtained is raised. For barrel-plating a lower ratio is desirable than when plating is carried out in

still vats, owing to the importance of good conductivity in such solutions, while a high caustic soda content is also desirable.

To improve the appearance of bright zinc deposits it is usual to use an after-dip as the zinc is sometimes covered with a brownish film. A suitable dip is a solution of hydrogen peroxide acidified with a little sulphuric acid similar to that used after cadmium-plating. (See p. 386.) A solution of chromic acid slightly acidified with sulphuric acid or a 1 per cent solution of nitric acid are similarly employed. Several proprietary bright zinc solutions are available employing special passivating and brightening after-dip systems. Very attractive finishes can be obtained, which are resistant to finger-marking and tarnishing to a much greater extent than normal zinc deposits. An improvement in the appearance of bright zinc deposits treated with chromic acid can be effected by a "bleach" treatment in an alkaline hydrosulphite solution.

The Zinc-Mercury Bath.—An older type of bright zinc deposit is that which makes use of an addition of a mercury salt to the usual type of cyanide solution. Only a very small proportion of mercury is necessary (approximately 0.04 oz. per gallon). The mercury content must not be allowed to become too high or spotty discoloration of the deposit may develop after a time. The solution is best operated warm (at about 100° F.), but satisfactory results are obtained at room temperature. The bath has good "throwing power" and covers well even at low current density areas. It is not too satisfactory for plating on to malleable or cast iron, while it should not be used for plating on to brass, as the mercury salts may initiate "season-cracking".

The anodes become amalgamated with the mercury in the solution when the vat is not worked, so that the mercury content of the bath must be replenished when recommencing deposition if the bath has been idle for any considerable period. The mercury is co-deposited with the zinc, but the corrosion resistance of the composite deposit does not appear to be affected. The deposit is, however, rather more prone to lead to corrosion when in contact with other metals than is a pure zinc deposit, due to electro-chemical action.

One advantage of the mercury type of bath is that the adverse effect of metallic impurities is much less marked than is the case with the other types of bright zinc deposits described owing to the fact that the mercury amalgamates with the metallic contaminants.

Very thorough washing of all types of zinc deposits (and especially of bright zinc) is essential if the plate is not to develop stains and discoloration.

ACID ZINC-PLATING

The acid zinc baths are considerably cheaper to operate than the cyanide solutions, but their "throwing power" is inferior while the deposits are somewhat coarser grained than those produced from the cyanide baths. On the other hand, deposits from acid baths are rather whiter in colour, while they are also more readily applicable

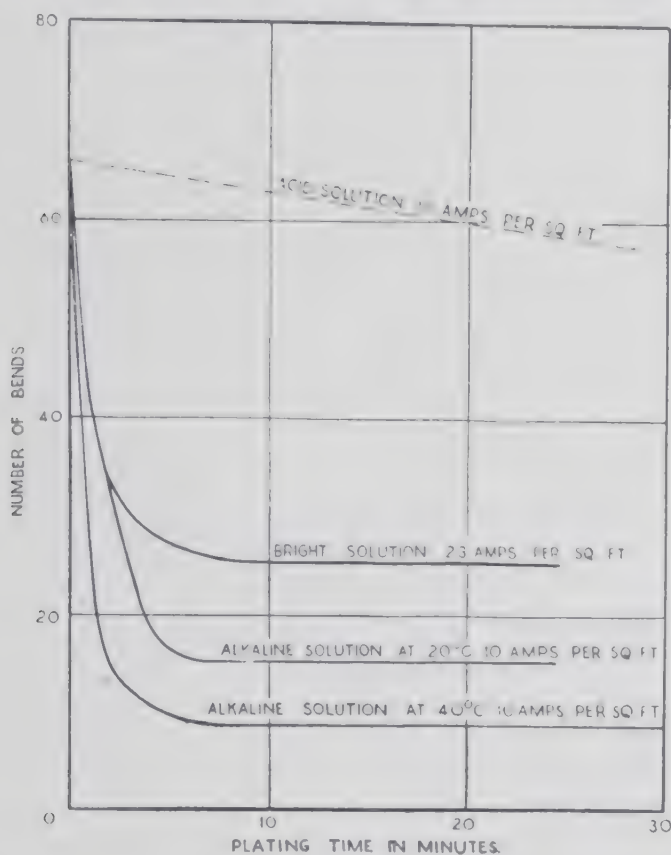


Fig. 120.—Effect of zinc deposits on bendability of spring steel strip

to deposition directly on to cast iron for which purpose cyanide solutions can only be used with difficulty. A less frequently noted, but none the less important, advantage of acid zinc-plating is the fact that deposits obtained from this type of electrolyte are much less prone to produce hydrogen embrittlement. Zinc-plating from cyanide solutions is notoriously liable to cause severe embrittlement, particularly of thin section steel of high carbon content (cf. p. 53).

Fig. 120 shows the results of some recent work in which zinc

deposits on spring steel sheets were subjected to repeated bending.⁽¹²⁾ Bending was carried out around a 5-mm. mandrel, the angle of bend being 180 degrees in each case. The number of bends which could be completed before the specimens fractured is seen to be considerably greater in the case of zinc deposits from the acid bath than those from the various alkaline solutions.

Electrolyte. The electrolyte used consists of an acid solution of zinc sulphate. The zinc sulphate concentrations are fairly high and vary from 40 to 60 oz. per gallon. Sulphuric acid is added to adjust the pH to about 3.5 to 4.5 (electrometric), but rather higher pH values (above 5.0) are employed for barrel-plating.

Increasing the acidity of the solution increases its conductivity, but the efficiency then falls. The anode efficiency of the solution usually exceeds 100 per cent since the acid in the electrolyte tends to dissolve the zinc chemically so that the pH of the solution steadily rises. At the same time basic zinc salts deposit on the anodes so that the rate of attack gradually decreases. Acid zinc solutions therefore increase gradually in metal content (unless an appreciable quantity is lost through heavy drag-out losses) while sulphuric acid must be added from time to time to keep the pH within the optimum working limits.

Chlorides (e.g. sodium, aluminium, or ammonium chloride) are often added to increase the conductivity of the solution, especially when barrel-plating is to be carried out. On the other hand, excessive amounts of these salts may have an adverse effect on the appearance of the deposits and on their corrosion resistance.

Organic addition agents are often employed in acid zinc-plating to improve the smoothness and lustre of the deposits and to enable increased current densities to be employed without leading to coarse-grained coatings. Certain of the addition agents also act as inhibitors and may help to reduce the tendency for the anodes to dissolve in the acid solution. Amongst the materials used are gelatin, dextrin, liquorice, sulphonated cresols and alcohols, and glycerine.

The following is a typical solution for use in a still tank:

Zinc sulphate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. . .	40 oz./gall.
Ammonium chloride, NH_4Cl . . .	$2\frac{1}{2}$ oz./gall.
Aluminium sulphate, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$. . .	5 oz. gall.

For barrel-plating, the following composition can be employed:

Zinc sulphate	80 oz./gall.
Aluminium chloride	3 oz./gall.

Operating Conditions.—Acid zinc solutions are best operated in rubber-lined steel tanks, but lead-lined, ceramic, or moulded synthetic resin tanks are satisfactory. Heating or cooling coils can be of hard rubber or lead-covered steel. The temperature should not be too high as at temperatures much in excess of 90° F. the deposits tend to become dark and coarse-grained when plating is carried out in still solutions. The "throwing power" is not too good, but sometimes adequate covering of deeply recessed articles can be



Fig. 121.—Section of hot galvanised zinc coating on steel wire, 0.92 oz. per sq. ft. ($\times 300$)

Courtesy of Rylands Bros. Ltd.

obtained by previously plating from a cyanide solution. The range of current densities employed in common practice is of the order of 20 to 40 amps. per sq. ft., but current densities of 1,000 amps. per sq. ft. and over have been used in the zinc-plating of wire in special plant (*vide infra*).

The cathode efficiency of the acid solution is very high and may exceed 98 per cent, while the anode efficiency often exceeds 100 per cent, as has already been mentioned.

The zinc anodes should be of high purity, since the presence of impurities may result in lowered cathode efficiency or in the formation of dark deposits of poor corrosion resistance. Also anodes of low purity may develop a coating of basic compounds of zinc, iron, lead, etc., which considerably reduces the amount of current which

can be passed through the bath without increasing the voltage. Improvement can then be effected either by cleaning the anodes or lowering the pH of the solution by the addition of acid.

The solutions are not generally filtered continuously, but periodic filtration is useful to remove suspended matter which can cause rough deposits. Under the usual plating conditions in still vats however, zinc solutions are not unduly sensitive, but in the plating of wire, for example, at high current densities, much more attention



Fig. 122.—Section of electro-galvanised steel wire, 0.96 oz. per sq. ft. ($\times 300$)

[Courtesy of Rylands Bros. Ltd.]

has to be given to the purity of the solution if successful results are to be obtained.

Electro-galvanising of Wire.—A most important development of recent years has been the introduction of electro-galvanising as a method of zinc-coating steel wire, in place of the older hot galvanising method. The process has the great advantage over hot galvanising in that no brittle alloy layers are formed between the zinc and the ferrous metal. These layers make the deposit somewhat prone to peeling when the wire is subjected to excessive deformation. As galvanised wire is usually subjected to considerable bending and twisting during subsequent fabrication operations the fact that electro-galvanised wire can withstand great stressing makes this type of coating particularly suitable for wire. The difference

between hot-galvanised and electro-galvanised wire is clearly seen in the sections shown in Figs. 121 and 122.

In the Tainton process which is being successfully operated on a considerable scale in this country, the zinc sulphate electrolyte is prepared by dissolving roasted zinc concentrates in sulphuric acid, precipitating the iron from the nearly neutral solution by manganese dioxide and then further removing metallic impurities electro-positive to zinc by the addition of metallic zinc powder.

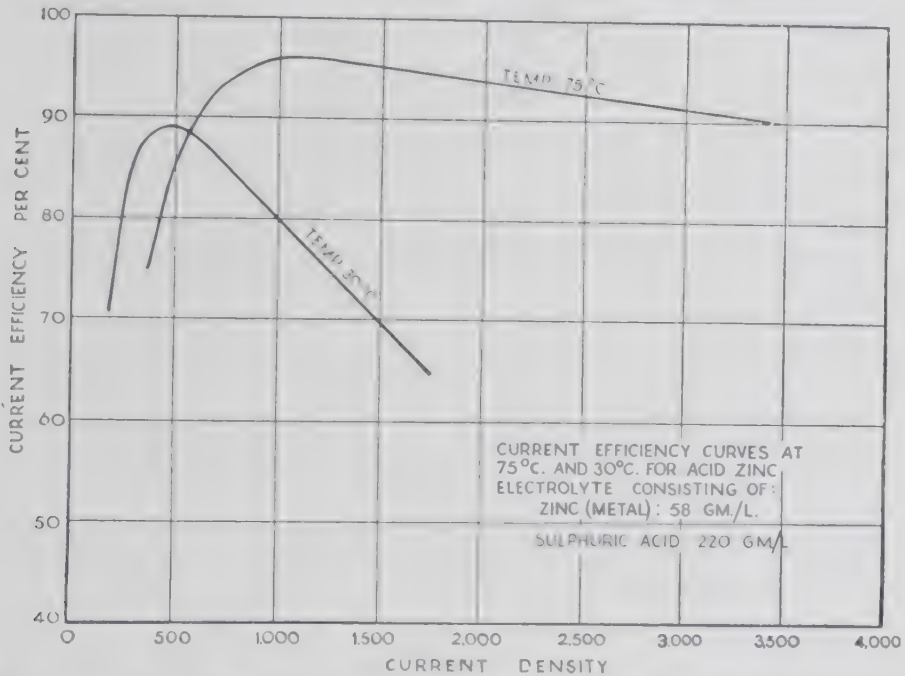


Fig. 123.—Current efficiency curves at 75°C. and 30°C. for acid zinc electrolyte consisting of: zinc (metal), 58 gm. per litre; sulphuric acid, 220 gm. per litre

During deposition the electrolyte is rather more acid than that employed in still tank plating since inert anodes are used. It consists of about 70 gm. per litre of zinc and up to 250 gm. per litre of sulphuric acid depending on the stage of electrolysis. The wire is first annealed at 700°C. in a lead bath and then carefully cleaned either cathodically in molten caustic soda or in a caustic alkaline solution. It is next anodically etched in a tank of the highly acid spent electrolyte and passes through a strike solution containing about 150 gm. per litre of zinc, before passing to the main plating cells.

The plating cells themselves are about 100 ft. long and the electrolyte is circulated continuously through them. They are of lead-lined steel and water-cooled to prevent excessive temperatures developing.

The efficiency of an acid electrolyte rises with increasing temperature over a wide range of current densities, as can be seen from the curves in Fig. 123, but the deposit is apt to deteriorate in appearance at the higher temperatures.

The current densities used are of the order of 800 to 2,000 amps. per sq. ft., depending on the size of wire being coated. Inert anodes of lead-silver alloy are employed, the silver content being of the order of 1 to 2 per cent. Lead anodes containing 2.5 per cent of silver are up to 25 times as resistant to the electrolyte as pure lead anodes, whilst these lead alloys are also much more tolerant of such impurities as bismuth, arsenic or antimony, which are very deleterious in lead anodes not containing silver. As deposition is carried out the electrolyte naturally increases considerably in acidity, as has been stated, while the metal content is depleted. This spent electrolyte is then employed for leaching further calcined zinc concentrates. A general view of the plant is shown in Fig. 124.

Thicknesses of zinc of up to 2 oz. per sq. ft. of surface are regularly deposited and the process is particularly suitable where it is desired to draw a thicker gauge coated wire down to a thinner gauge after plating. In this way a compact coating with a high finish can be obtained. The deposit is of high purity (exceeding 99.99 per cent zinc) and is so ductile that the finished wire can be wrapped round its own diameter without fracturing the coating or loosening it from the steel.

The purity of the electrolyte in the electro-galvanising of wire is important. Copper must be kept below 0.009 gm. per litre, or the deposit will tend to become spongy, while the current efficiency will be lowered. Iron has a similar effect in concentrations greater than 0.05 gm. per litre. A particularly obnoxious constituent of acid zinc electrolytes appears to be germanium, which in concentrations as low as one part in 10 million will markedly reduce the current efficiency.⁽¹³⁾ The process has been fully described by Roebuck and Brierley as operated in this country.⁽¹⁴⁾

Another application for continuous electro-galvanising is in the plating of steel strip for many purposes. Of particular interest is the coating by this method of narrow strip; this is subsequently formed and coiled on interlocking machines for the manufacture of flexible metallic tubing, which has multifarious applications. It is important for this application that a highly adherent and flexible coating be produced to enable it to withstand the very severe forming operations involved in the manufacture of this type of tubing.

The Fluoborate Zinc Bath. The use of fluoborate baths for the deposition of many metals is becoming of increasing importance as

they enable high rates of deposition to be obtained both in automatic and manually operated plants. The solutions are used at room temperature and have high anode and cathode efficiencies. They also give good deposits of excellent colour on cast iron, which is a considerable advantage.



Fig. 124.—General view of plating cell for electro-galvanising steel wire

Courtesy of Rylands Bros. Ltd.

A solution for the high-speed plating of wire, sheet and strip which has been recommended consists of:

Zinc fluoborate	50 oz./gall.
Ammonium chloride	4.5 oz./gall.
Ammonium fluoborate, NH_4BF_4	6 oz./gall.
Liquorice	0.2 oz./gall.

A pH of 3.5 to 4.0 is used. By increasing the temperature the resistance of the bath is reduced so that it is more suitable for high-speed plating, although the throwing power is poorer.

A more dilute version of this bath is used for plating in still tanks. the anode area should be about double the cathode area.

Properties of Zinc Electro-deposits.—Zinc deposits are finding increasing application for rust protection, particularly where the greater uniformity of such deposits over those obtained by hot-galvanising is appreciated. In certain fabricated assemblies the low temperature at which the electro-plating process is carried out eliminates the tendency to distortion which is noticeable in hot galvanising.

As an undercoat for paint from the adhesion point of view electro-deposited zinc is more satisfactory than is a hot-galvanised coating. The adhesion of paint to the former is not perfect and if really first-class adhesion be required a preliminary phosphate or chromate treatment of the zinc is desirable; even without such pre-treatment, however, the adhesion is markedly superior to that obtained on hot-galvanised coatings. Electro-galvanised steel sheet and strip are now being manufactured on a substantial scale, and find considerable application where a high degree of protection against corrosion and abrasion are required. The plated metal carries from 0.0001 in. of zinc and upwards, and is available in the phosphated condition ready for painting. Sheared edges present no great problem as not only is there a good degree of anodic protection by the zinc itself in the case of relatively thin sheet, but there is little tendency for any corrosion that may occur on the edge itself to spread over the metal surface.

Hudson and Banfield⁽¹⁵⁾ as a result of considerable exposure tests on zinc and cadmium deposits claim to have developed formulae for the useful service life of such coatings in industrial atmospheres. These formulae are:

$$\begin{array}{llllll} \text{Cadmium} & . & . & . & . & . & L = 1.1w + 0.1 \\ \text{Zinc} & . & . & . & . & . & L = 2.6w + 0.5 \end{array}$$

where L = life of coating in years to failure (5 per cent of surface rusted) and w = weight of coating (oz. per sq. ft.).

CHROMATE PASSIVATION

Zinc deposits are prone to develop white corrosion products of basic zinc salts under conditions of humidity. Dipping in an acid solution of sodium dichromate markedly improves the properties of the deposit in this respect (see p. 215). In the Cronak process described by Anderson⁽¹⁶⁾ a solution consisting of:

$$\begin{array}{llll} \text{Sodium dichromate} & . & . & 200 \text{ gm. per litre} \\ \text{Sulphuric acid} & . & . & 6 \text{ to } 9 \text{ c.c. per litre} \end{array}$$

is used for immersion.

A film is produced which is highly protective and inhibits the formation of a white corrosion product which normally appears on zinc in time. In this way it usefully improves the life of zinc or zinc-plated parts, particularly those constituting moving members of mechanisms where corrosion may cause failure. The process can also be applied to cadmium, but its advantages here are much less marked.

The effectiveness of the film depends on the liberation of hexavalent chromium to the extent of 0.0001 to 0.0005 gm. per litre in water in contact with it; the film does not appreciably add to the life of zinc exposed to outdoor weathering, owing to the rapid leaching out of the chromium compounds which occurs under the latter conditions. The application of the process should, therefore, be limited to those components subject to condensation and humidity, but protected from the outside weather.

Method of Treatment.—If plated work is being treated the dip can be carried out immediately following the washing treatment after plating; the work is immersed in the treatment solution for about ten seconds, after which it is removed, drained for not more than thirty seconds, and rinsed thoroughly in cold running water. At least two rinse tanks are required to ensure that all traces of residual chromate are removed; the last rinsing water should not show yellow. If the solution is not completely removed the effectiveness of the treatment will be greatly reduced. The rinsing water should be cold. The work is finally dried off by means of a blast of cool air or by suspension in a tunnel or duct through which air passes at a velocity of 25 to 35 ft. per sec. Drying at elevated temperature is unsatisfactory, since it results in the formation of hard films which have poor protective value.

Defects in the Film.—The time of immersion determines the appearance of the film. With a very short immersion time iridescent films are produced. As immersion time increases iridescence lessens and a golden-brown colour develops. If the time is too long the film may become chalky; such films are less abrasion-resisting and more difficult to dry. The best colour is golden-brown with some iridescence.

The colour depends not only on the composition of the solution, temperature, etc., but also on the texture of the zinc surface. Thus, films on bright surfaces tend to be more resistant than those formed on matt surfaces, whilst if the zinc contains copper a strong green colour develops; within reason such colours are not detrimental to the protective quality of the film. With experience, however,

operators treating standard zinc surfaces soon become accustomed to the correct appearance of a good film and can readily reproduce it. If good films are not obtained in a reasonable time three factors may be responsible:

- (a) The temperature of the bath may be incorrect. The films form very slowly at temperatures below 70°F. , and sometimes not at all below 60°F. , but, on the other hand, temperatures which are above 70°F. cause chalky, poorly adherent films to be obtained.
- (b) If the sulphuric acid content is low, poor films will be obtained; sulphuric acid is consumed during the progress of the treatment, and its concentration must be maintained by suitable additions, as will be described below.
- (c) If the work is not properly cleaned, unsatisfactory films will be obtained.

The drying time should not be unduly prolonged as if the solution dries on the work an unsatisfactory finish will be obtained, although attack on the zinc ceases when the work is withdrawn from the solution. The treatment results in a slight removal of metal from the surface, and this loss ranges from 0.000003 to 0.0001 in., depending on the conditions of immersion. The latter figure is extremely high and is seldom reached.

Maintenance of Solution.—The solution can be maintained by chemical analysis of the constituents. An alternative empirical method is to withdraw an aliquot proportion of the bath and add sulphuric acid until samples dipped into it under the proper conditions become covered with a satisfactory film; the same percentage additions are then made to the main bath; normally, two or three additions of acid can be made before the solution reaches the point where it must be discarded. It is not advisable to add sodium dichromate, since by the time this constituent requires renewal it is no longer practicable to regenerate the bath.

Unsatisfactory films may be stripped by immersion in a boiling solution containing 200 gm. per litre of chromic acid for several minutes. Prior to re-treatment the parts may have to be passed through an alkali-cleaning cycle.

The process has been studied more recently by Clarke and Andrew,⁽¹⁷⁾ who found that the dichromate content of the solution can be varied widely without ill effect. The acid concentration, on the other hand, must be carefully controlled, as too little acid gives

films too thin for normal purposes, whilst excess acid concentration results in poor adhesion of the film and unnecessary attack on the zinc. The period of immersion should not be unduly prolonged. They confirm Anderson's findings that heating the film or treating it with hot water reduces its protective value. The film contains 20 to 30 per cent of water and dehydration by heating results in an increase in its permeability, perhaps due to shrinkage or cracking and a loss in the solubility of the deposit; keeping, however, does not appear to cause dehydration. Poor protection is often associated with too great a thickness of film or a powdery deposit.

Anodic Conversion Coating.—It is also possible to produce adherent coatings by anodic treatment in chromate electrolytes. In the "Anozinc" process the parts are subjected to treatment for 10 amp. minutes per sq. ft. when a yellow coating said to consist of zinc oxide and chromate is formed.⁽¹⁸⁾ A typical solution recommended consists of:

Sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$	200 gm./l.
Na_2SO_4	5 gm./l.
pH	3 to 4.5
Temperature	70° F.

It is claimed that the coatings obtained in this way are very adherent and are not detached by sharp bending. They will therefore withstand cutting and shaping operations on the metal. Furthermore, these coatings are more uniform in colour and harden more rapidly than those produced by the immersion treatment.

Plant Construction.—The tanks for the process may be made of ordinary black iron. Slow attack may take place, but a reasonable life is to be expected from them. Much better durability is, however, obtained with tanks which are made of stainless steel or earthenware.

The parts should preferably be racked for treatment, as bulk immersion in baskets may result in the abrasion of the film, which is rather soft while wet; it may also make rinsing more difficult. In some instances, however, such as on parts free from recesses, bulk treatment in baskets is satisfactory.

LEAD-PLATING

Lead-plating has not, in the past, received any great attention as a rust-proofing coating because of the ready availability of zinc and cadmium, which are generally considered to be superior in this respect. It is not normally possible to apply lead to steel satisfactorily by dipping unless some tin or other suitable metal is alloyed with

it to promote wetting of the base metal. The electro-deposited metal is not, however, subject to this limitation, and is often less porous than hot-dipped coatings of equal thickness. Where resistance to sulphuric acids is concerned, as in the manufacture of lead accumulator fittings and acid-containing fire-extinguishers, electro-deposition affords the best means of producing the pure lead covering which is desirable for maximum serviceability, both on ferrous and non-ferrous metals.

Types of Bath.—There are two baths commercially utilised for lead deposition, viz. the fluosilicate and the fluoborate baths, although recently the lead sulphamate solution has been receiving some attention in the U.S.A. (cf. p. 407). The first of these is employed principally for electro-refining and is not really suitable for the application of protective lead coatings. It suffers, moreover, from the disadvantage that the solution will not plate directly on to steel, a copper undercoat being essential.

The Fluoborate Bath.—To all intents and purposes, the only present-day bath of interest to the electro-plater is the fluoborate bath. Gray and Blum⁽¹⁹⁾ recommend the following solution for the deposition of good lead deposits up to 0.05 in. in thickness, or for barrel-plating:

Basic lead carbonate, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$	.	.	300 gm. l.
Hydrofluoric acid (50 per cent HF)	.	.	480 gm. l.
Boric acid, H_3BO_3	.	.	212 gm./l.
Glue	.	.	0.2 gm./l.

A bath of half the above concentration is suitable for thinner deposits at low current densities, but the lead concentration should be kept high if smooth deposits and good throwing power are required. The solution is best operated in a rubber-lined steel tank, but lead-lined and wood tanks are also used. Lead is not attacked by the solution, but an inner glass or plastic lining is advisable to prevent the lining becoming anodic or cathodic accidentally. Ceramic or synthetic resin tanks are also suitable.

Although the best operating temperature is from 80° F. to 100° F., the bath is commonly used at room temperature. The current density range is from 10 to 30 amps. per sq. ft., depending on the composition of the solution and on the thickness of deposit required. The cathode efficiency of the bath is high, being in the region of 98 per cent. The rate of metal deposition at various current densities is shown in Fig. 125. A low current density range of 5 to 15 amps. per sq. ft. is preferred where uniformity of coating is

required. With light cathode rod agitation the solution can be operated successfully at considerably higher current densities and figures of 80 amps. per sq. ft. have been reported. The solution has good conductivity and only relatively low voltages are needed, up to 2 volts being sufficient for plating in still solutions, while 4 to 6

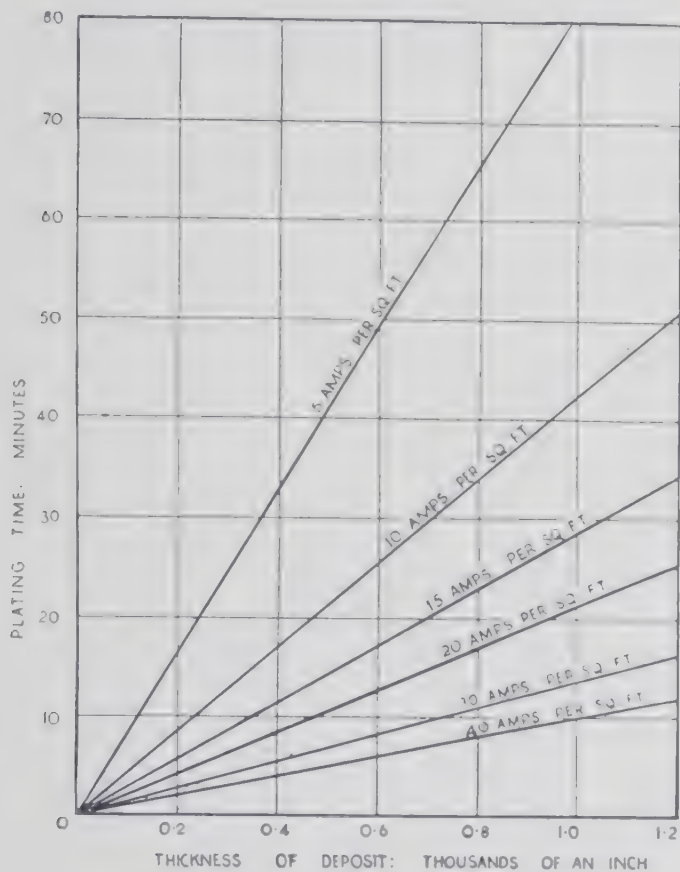


Fig. 125.—Rate of deposition of lead

volts may be necessary in barrels. High voltages are to be avoided, as they tend to cause “treeing” of the deposit.

Some Characteristics of the Solution.—It is generally assumed that in the preparation of the solution the hydrofluoric and boric acids interact in accordance with the following equation:



The lead in the fluoborate bath is in the form of lead fluoborate, $\text{Pb}(\text{BF}_4)_2$, but there is generally an excess of lead dissolved in the solution over and above the requirements of this formula. In

operating the bath an excess of fluoboric acid is maintained in the solution; a proportion of boric acid (about 10 to 15 gm. per litre) over that required theoretically to form the compound HBF_4 is also usually added. The "free" fluoboric acid serves to reduce the tendency of the deposit towards "treeing" and improves the conductivity of the solution. The excess boric acid improves the stability of the bath, reducing the tendency for decomposition to take place with the precipitation of lead fluoride; this can occur if any excess of hydrofluoric acid should develop in the bath.

The control of the pH of the solution is also advisable, and a value of 1.0 to 1.5 (electrometric) is a good range in which to work. This is maintained by the periodic addition of fluoboric acid.

In making up the bath the boric acid is gradually added to the hydrofluoric acid in a suitable tank, after which the basic lead carbonate in the form of a paste is stirred in slowly. After diluting to the correct concentration the solution is carefully filtered, the addition agent is added, and the bath is ready for use. The free fluoboric acid is maintained by an empirical titration with decinormal caustic potash, and additions of boric acid and hydrofluoric acid mixed together in the proportions of 1 to 4 are made from time to time.

Addition Agents. Various addition agents have been experimented with to reduce "treeing", to which lead solutions are especially prone, glue being most widely used. The presence of some addition agent is essential if fine-grained deposits are to be obtained and the tendency towards "treeing" obviated. In some early experiments by Blum⁽²⁰⁾ it was found that 800 gm. of lead could be deposited from 1,200 c.c. of fluoborate solution containing 0.2 gm. l. of glue before "treeing" became evident, and even thereafter the tendency towards "treeing" was much reduced.

Other addition agents which have been proposed are gelatine and phenolic compounds, such as pyrogallol and resorcinol, but glue is most commonly used in industrial practice. The grade of glue must be of high quality, and its effect on a small amount of the solution should be tested before it is added to the bulk. A throwing power test is a very satisfactory guide, while a microscopic examination of the deposit under a magnification of about 500 is also of value. The use of an unsuitable grade of glue or an excessive concentration will reveal many dark-coloured inclusions, and in some cases a powdery appearance on the surface of the deposit.⁽²¹⁾

Anodes. The anodes used should be as pure as possible, chemical lead being most satisfactory. The anode efficiency is about 100 per

cent. Impure anodes can cause anode films and sludges, which interfere with the formation of smooth and uniform deposits. Copper is particularly to be avoided in the anodes; as little as 0.08 per cent appears to have an adverse effect on the deposit.

Cleaning.—Cleaning of steel prior to lead-plating is similar to that used for other metals, but over-pickling must be avoided. Where a sulphuric acid pickle is employed, thorough rinsing is essential as the introduction of sulphuric acid into the solution results in the immediate precipitation of some of the lead as lead sulphate. Similarly, any water added for topping up the bath should be substantially free from sulphate. Shot-blasting is often advisable for badly scaled parts, and on occasion a deposit of copper may be applied to promote adhesion of the lead. Lead-plating from this bath has little or no embrittling influence on steel.

Alternative Baths.—Although practically all lead-plating being carried out commercially in this country makes use of the fluoborate solution, two other baths are worthy of note:

The Perchlorate Bath.⁽²²⁾ This bath is prepared by dissolving lead oxide in perchloric acid, the solution containing about 50 gm. per litre of lead with an equal amount of free perchloric acid (HClO_4). The addition agent used is peptone, or, less satisfactorily, clove oil, to the extent of about 0.5 gm. per litre. Good deposits can be obtained from this bath.

The Sulphamic Acid Bath.⁽²³⁾ Excellent results are said to have been obtained in the U.S.A. from this solution, which is prepared by dissolving an excess of basic lead carbonate in a 5 per cent solution of sulphamic acid (HSO_3NH_2), filtering off the excess and then adding a further 5 per cent of sulphamic acid. The resulting solution has a pH of 1.0 to 1.5. Addition agents are necessary, among those recommended being: (a) 0.07 per cent of beta-naphthol and 0.7 per cent of aloin; (b) 0.05 per cent of casein and 0.1 per cent of aloin; (c) 0.5 per cent of malic acid and 0.1 per cent of aloin; (d) 0.7 per cent of glue and 0.07 per cent of beta-naphthol. The current density which can be employed is of the order of 20 amps. per sq. ft., while the cathode efficiency is over 95 per cent.

Resistance to Corrosion.—Lead deposits of 0.0005 to 0.0010 in. in thickness give good protection against corrosion if substantially non-porous, but, owing to the soft nature of the metal, breaks in the coating occur relatively easily if it be subject to abrasion; owing to the fact that lead is cathodic to iron, rusting at such breaks occurs more readily than with zinc-plating. It is, however, less cathodic than copper to iron, while in a marine atmosphere there is some

evidence that it may be weakly anodic.⁽²⁴⁾ With lead deposits heavier than 0.0010 in. the mechanical properties of the coating are improved so that better durability is obtained. In depositing lead on articles of involved shape it should be borne in mind also that the solution has much poorer throwing power than have zinc- or cadmium-plating solutions.

For the testing of the porosity of lead deposits, Gray and Blum recommend washing the plate in 10 per cent sulphuric acid to remove particles of iron or iron oxide on the metal surface and treating with a solution of 20 gm. l. of sulphuric acid and 10 gm. l. of potassium ferricyanide. Bright blue spots appear within a minute to indicate the presence of pores in the coating.

Thin copper coats under the lead do not materially improve the corrosion resistance of thin coatings, but coatings of 0.0005 to 0.0010 in. are valuable as undercoats. A copper undercoat is also useful when soldering has to be carried out on to the lead deposit.

In some exposure tests carried out by Clarke⁽²⁵⁾ at Woolwich, steel sheets carrying lead deposits 0.0001 in. thick were completely rusted in six months; deposits 0.0005 in. thick had small rust patches in one year, while coatings of 0.001 in. thickness were highly protective, showing no rusting or apparent deterioration at the end of three years.

In contact with zinc or aluminium, in particular, acceleration of the corrosion of the coating tends to occur and such contact is best avoided.

Lead deposits of 0.003 in. or more are relatively easily built up, and have a high degree of durability. For example, in one hour at 20 amps. per sq. ft. a deposit of about 0.004 in. can be produced, which is roughly about three times as thick as a nickel or a zinc deposit plated at the same current density and for a similar period.

Alloys. --Blum and Haring⁽²⁶⁾ have described the deposition of fine-grained, lead-tin alloys from the fluoborate bath. The ordinary lead fluoborate solution is used, the tin being introduced by electrolysis of the lead solution with tin anodes until the requisite amount of tin is present in the solution. It is not practicable to attempt to make tin fluoborate. Owing to the preferential dissolution of tin from the anode it is desirable to work with lead-tin anodes containing rather less tin than that which is required in the deposit.

It is quite practicable to operate this bath within the range of 25 to 75 per cent of tin by weight and maintain a constant alloy composition, but below this tin content the composition of the deposit and the corrosion of the anodes vary so irregularly with

slight changes in current density that the operation of the solution becomes impracticable.

Very little is known regarding the behaviour of electro-deposited coatings of this type under conditions of atmospheric exposure, although it is to be expected that this will be similar to that of terne-plate.

Lead Alloys for Bearings.—Lead is frequently deposited on steel to produce bearings for aircraft and other heavy duty applications. Increased durability of the thin lead deposit (which is usually about 0.0003 to 0.0005 in. thick) is obtained by further depositing a tin or indium layer on to the lead and infusing the latter deposit into the former by heating the bearing in an oil bath at about 170° C. This results in alloy formation at the bearing face which increases its resistance to the corrosive effect of hot oil. The large scale production of such bearings has been described by Wright.⁽²⁷⁾

The application of lead alloy bearing surfaces to non-ferrous metals presents a special problem. The use of such electro-deposits for improving the performance of high-pressure aluminium-bronze fuel pumps has been described by the author.⁽²⁸⁾

Protective Value.—Some more recent investigations on the protective values of lead and of lead-tin alloy deposits on steel have been carried out by du Rose.⁽²⁹⁾ The results indicate that these deposits can, in some cases, give protection as good as that afforded by zinc- or cadmium-plating. Owing to the inferior throwing power of the lead solution, however, low current density areas are apt to be poor. If pin-holes occur in a lead deposit rust appears, but this is often covered up by the corrosion products of the lead. A copper flash (0.00005 in.) improves the durability of lead-plated steel if the lead is 0.0001 to 0.0005 in. thick. Thinner deposits of copper may be detrimental, whilst if the lead coating is thicker than 0.0005 in. the useful influence of the copper is not very evident.

The effect of the glue concentration in the plating bath is very marked under salt-spray test, and there is a considerable advantage to be gained by increasing it above that usually employed. A glue content of 0.2 per cent or more is recommended.

With regard to the effect of tin, there is a gradual increase in the protective value of lead-tin alloys as the tin increases up to 5.5 per cent; 10 per cent, and 15 per cent tin alloys are comparable with a 100 per cent tin deposit from an acid sulphate bath. Also the lead-tin alloy deposits are lighter in initial colour and after exposure than are those of pure lead.

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THICKNESS

To a very considerable extent the protective values of many coatings, and particularly of electrodeposits, are a function of their thickness and all specifications include a thickness requirement.

The measurement of the thickness of an electro-deposit can be carried out in several ways.

Microscopic Method. The most accurate method of determining the thickness of coating is to prepare a section of the specimen by cutting and polishing, after which the thickness is measured under the microscope. The sample is best moulded into a plastic matrix or embedded in a low melting alloy to prevent flow of the coating during polishing when soft metals such as zinc or cadmium are being dealt with. It is essential, however, to ensure that the section is truly normal to the deposit, otherwise considerable errors may result. This method is, however, slow and expensive and is only employed for special purposes.

Chemical Methods. It is possible to dissolve the coating from the basis metal and to determine the amount of metal present in the solution by chemical analysis and hence to calculate the thickness of the deposit. This is seldom carried out, however, since it is simpler to select a treatment which will dissolve the deposit from a given area without affecting the base metal. By weighing the specimen before and after stripping, the weight and hence the thickness of the deposit can be readily determined.

Nickel can be dissolved by anodic dissolution in 70 per cent sulphuric acid using a current density of about 20 amps. per sq. ft. This method is applicable to deposits on steel, copper, brass and zinc-base alloys. It is, however, difficult to ensure absolute freedom from attack especially on steel, so that it is not very accurate. Another method has been suggested by Mears⁽¹⁾ in which the deposit is made the anode in a 20 per cent solution of sodium cyanide. The steel is not attacked but passivity may develop in the nickel; should this occur the current is momentarily reversed and the process continued.

Chromium is best stripped anodically in caustic soda solution from all base metals except zinc, when sodium carbonate solution should be used.

Zinc, Cadmium, and tin are stripped from steel by means of a strong solution of hydrochloric acid containing a small amount of antimony trioxide which acts as an excellent inhibitor of attack on the basis metal. Cadmium and zinc are also readily removed from steel by a 5 per cent aqueous solution of ammonium persulphate to

which is added 10 per cent by volume of ammonia (sp. gr. 0.880). In the case of zinc a hot sodium polysulphide solution made up from 250 gm. per litre of sodium sulphide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) and 25 gm. per litre of sulphur is satisfactory.

Copper deposits are removed from steel by means of a chromic acid solution containing about 500 gm. per litre of chromic acid and 5 gm. per litre of sulphuric acid. The solution is best used hot. Nickel or copper or both can also be removed from steel by anodic treatment in sodium nitrate solution. The solution is fairly concentrated (80 oz. gall.) and is kept at a pH of 7.6 to 8.2. It is used at a current density of 200 amps. per sq. ft. at 6 volts, and a steel cooling coil is required in the solution to prevent overheating by the large currents used.

Anodic stripping can be satisfactorily carried out in a solution consisting of:

Copper cyanide	.	.	.	40 gm./l.
Sodium cyanide	.	.	.	80 gm./l.
Trisodium phosphate	.	.	.	60 gm./l.
pH	.	.	.	12.2

The solution deteriorates rapidly, however, if large anodic areas of steel are exposed due to the formation of carbonates and the decomposition of cyanides. The former must be removed and the latter replaced if the bath is to be regenerated. The pH should be controlled at between 11.9 and 12.5 by the addition of caustic soda; the presence of cyclohexylamine in combination with sodium sulphite has been found to be effective in prolonging the life of the bath.⁽²⁾

Copper, brass, bronze, cadmium, zinc and also gold and silver can be stripped anodically in a solution containing sodium cyanide, 1 lb. per gallon and caustic soda $2\frac{1}{2}$ oz. per gallon.

Silver deposits on brass or nickel silver can be removed by immersion in a bath of hot concentrated sulphuric acid containing 5 per cent by volume of concentrated nitric acid.

Lead can be removed from steel by dissolution in a mixture of acetic acid and hydrogen peroxide used at room temperature. A suitable bath consists of:

Acetic acid	.	.	.	10 per cent
Hydrogen peroxide	.	.	.	10 to 20 per cent

Small additions of hydrogen peroxide should be made from time to time to keep the solution active.

Gold can be dissolved from copper, brass, steel or nickel alloy

surfaces by treatment in a sodium cyanide-hydrogen peroxide bath, small amounts of hydrogen peroxide being added as required to a solution containing about $\frac{1}{2}$ lb. of sodium cyanide per gallon of water.

Chord Method.—In this method a circular grinding wheel is applied to the coating until it is cut through. The thickness can then be calculated from the formula:

$$T = C^2/8R,$$

where T is the thickness of the deposit, C is the width of the cut, and R the radius of the wheel. The method is limited by the fact that a precision grinder is required for flat surfaces, but it can be applied to curved surfaces by using a fine flat file if the radius of curvature of the surface is known. It cannot readily be used on concave surfaces.

B.N.F. Jet Test.—In this country the B.N.F. Jet Test is now the most widely used method for the routine measurement of plating thicknesses.⁽³⁾ In this method a jet of a specified reagent is directed on to the coating under carefully standardised conditions and the time for penetration determined. Suitable solutions are available to enable this method to be applied to nickel, copper, zinc, cadmium and silver deposits on most of the commonly employed base metals. The jet is directed on to the carefully cleaned article under a constant head of 10 in. The characteristics of the jet have been defined in a British Standard Specification (B.S.S. 1224 : 1945). It should consist of a glass capillary tube of 1.5 mm. circular bore, not less than 4 in. in length drawn out into a smooth taper at the nozzle end and ground off flush at the tip of the nozzle. The dimensions of the tapered portion should be such that $\frac{D-d}{L}$ must be between 0.030

and 0.045 where D is the internal diameter of the capillary tube, d the internal diameter of the nozzle tip and L the length of the taper. The jet must deliver 10 ml. of water at 20°C. in 27 to 29 seconds under a 10 in. head. For nickel, the test solution consists of:

Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$)	. . .	300 gm./l.
Copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)	. . .	100 gm./l.

When penetration has occurred a copper spot appears in the case of nickel deposits direct on steel. As this is not visible whilst the jet is running the latter must be stopped from time to time to ascertain whether penetration has occurred; a seconds clock is started and stopped during the test to obtain a measure of the total time during which the jet is actually running. The time of penetration is dependent on the temperature of the solution as shown by

a thermometer immersed in the reservoir. Fig. 134 shows a suitable apparatus for the test consisting of a container for the fluid with a stop-cock, a constant head device with thermometer, a shielded jet and a clamp for holding the specimen.

On brass and zinc-base alloy die-castings a black spot appears

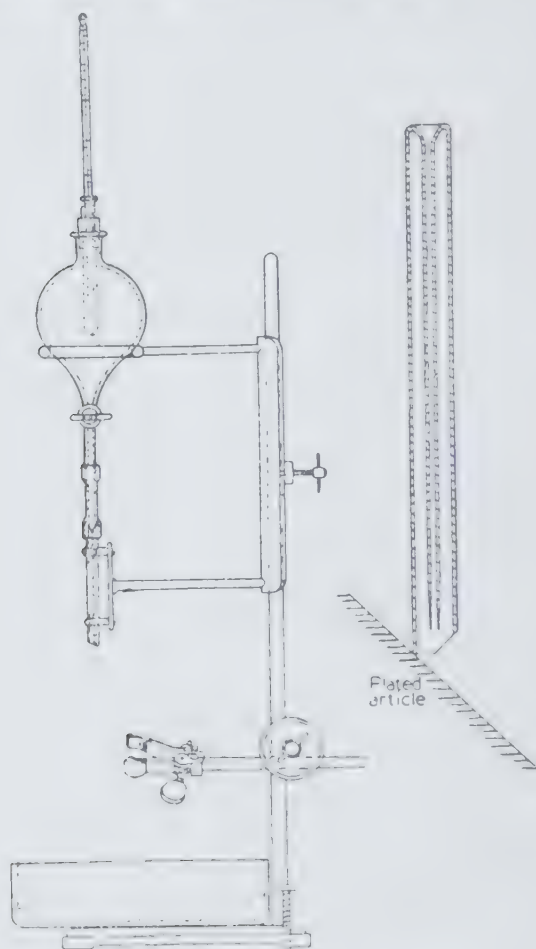


Fig. 134.—B.N.F. jet test apparatus

when the coating has been penetrated. Where the nickel is on a copper undercoat on steel, penetration of the latter is shown by the periodic application to the spot of a drop of a 1 per cent solution of antimony trioxide in a 1 : 1 per cent solution of hydrochloric acid. A black spot indicates penetration.

For cadmium the solution used consists of:

Ammonium nitrate	17.5 gm./l.
Hydrochloric acid (normal)	17.5 c.c./l.

whilst for zinc a solution four times as concentrated as the above is used. In this case penetration is complete when steel shows through the coating. This is a little more difficult to see.

The difficulty in observing the end-point in the case of cadmium deposits on steel can be overcome by applying one or two drops of a solution consisting of 10 gm. of mercuric chloride and 50 c.c. of concentrated hydrochloric acid per 100 c.c. of water to the test spot. The effect produced is a bright mercury spot at the point of exposure of the steel, the surrounding cadmium being blackened. If the solution has been applied before perforation has been reached the jet test should be recommenced at another spot.

In the case of zinc the end-point can be similarly confirmed by applying one or two drops of a solution containing 20 gm. of potassium ferricyanide and 20 c.c. of concentrated hydrochloric acid per 100 c.c. of water to the spot, when a local brick effervescence occurs at the point of exposed steel, the surrounding zinc surface being coloured brown. This test is not satisfactory for cadmium deposits.

Charts showing rates of penetration are given by Clarke (*loc. cit.*). At 25° C. 4.2 seconds are required to penetrate 0.0001 in. of nickel and 2.2 seconds for the same thickness of copper with the ferric chloride solution.

In the case of the ammonium nitrate solution 0.0001 in. of zinc is penetrated in 4.0 seconds and a similar thickness of cadmium in 9.4 seconds at 25° C.

More recently the test has been extended to silver deposits.⁽⁴⁾ The solution used consists of 250 gm. per litre of potassium iodide and 7.44 gm. per litre of iodine. Silver is dissolved at the rate of 0.0001 in. in 5.6 seconds at 25° C., and in 6.6 seconds at 18° C. The end-point is shown by the development of a bright crescent-shaped area of the underlying metal.

The thickness of *lead deposits* can be determined by the use of a solution consisting of:

Glacial acetic acid	.	.	.	1 vol.
Hydrogen peroxide (5% H_2O_2)	.	.	.	1 vol.
Distilled water	.	.	.	3 vol.

The strength of the peroxide is standardised by titration against potassium permanganate from time to time as the solution is somewhat unstable. The method is applicable to lead coatings on steel or silver; the specimens should be free from grease or oxide films before test.⁽⁵⁾

The Jet Test is accurate to about 15 per cent, which is sufficient for inspection purposes.

Dropping Test.—A similar method employed extensively in the U.S.A. consists in using an apparatus designed to give a series of drops instead of a jet of solution. The drops fall at the rate of 100 per minute, and the thickness of deposit is again a function of time and temperature.

Electrolytic Thickness Tester.—An electrolytic thickness testing apparatus has been described by Francis.⁽⁶⁾ The principle of the instrument is the anodic dissolution of an area of the plated metal, the current-time product being determined and used as a measure of thickness. The stripping current is held constant during the test, and the end-point is defined by a sharp rise in cell voltage which occurs when the coating metal has been removed. A relay is incorporated in the circuit, which stops a timing clock and causes an indicator bulb to light up. The stripping time is converted to plate thickness, either by direct calculation from the current time, area stripped and the equivalent weight of the metal, or from a chart of the stripping time plotted against plate thickness. The method is suited to very thin coatings.

The electrolytes used are either 10 per cent sodium hydroxide or 10 per cent potassium cyanide. The alkali-soluble metals include tin, lead, zinc and chromium, and the cyanide-soluble metals are cadmium, copper, silver, gold and brass. The base metal can be steel, brass, copper or certain other metals.

Chromium. The thickness of a chromium deposit can be measured by noting the time required for a drop of hydrochloric acid (sp. gr. 1.160) containing 20 gm. l. of antimony trioxide to dissolve the deposit. To prevent the acid from spreading it is applied inside a ring of paraffin wax applied to the plated surface.

Again the rate of dissolution is dependent on temperature; Table XXXVII shows the rate of attack over a range of temperatures.

Preece Test.—This test is sometimes specified as a means of determining the minimum thickness of a zinc coating on steel. The specimen is immersed in a copper sulphate solution for a given time. The absence of an adherent copper deposit indicates that the coating is satisfactory. The test is inaccurate and has little to commend it.

Time of Gassing Test for Cadmium.—A simple test for cadmium thickness has been proposed by Clarke and Andrew.⁽⁷⁾ A solution consisting of 10 gm. of nickel-sulphate crystals dissolved in 100 c.c. of hydrochloric acid (sp. gr. 1.16) is applied to the cleaned surface at a temperature between 15° C. and 25° C. The thickness of cadmium

TABLE XXXVII

RATE OF DISSOLUTION OF CHROMIUM IN HYDROCHLORIC ACID

Temperature °C.	Time to dissolve 0.0001 in. (secs.)
18	11.5
20	10.3
22	9.3
24	8.3

is obtained by dividing the time in seconds before a marked decrease in the rate of gassing takes place by 3.9. This gives the cadmium thickness in ten thousandths of an inch.

Magnetic Methods.—Several types of magnetic gauges have been developed for thickness testing. They are all limited, however, by the fact that they can only be used to measure the thickness of magnetic coatings on non-magnetic bases and vice versa.

In all the types of apparatus that have been described⁽⁸⁾ the general principle is that the force of a permanent magnet placed on the coated surface actuates a spring which records on a calibrated dial. In the case of a magnetic deposit, such as nickel on brass, for instance, the force will depend on the thickness of the nickel; with non-magnetic coatings, on the other hand, the thicker the intervening layer the less will be the force between the magnet and the underlying metal. It is also possible to use such an instrument for the measurement of nickel coatings on steel because of the weak magnetic properties of nickel in comparison with those of steel.

An electro-magnetic method has also been developed for the measurement of the thickness of non-magnetic coatings on steel.⁽⁹⁾ In this case an ammeter records the amount by which the flux of a magnetic circuit is reduced when it comes between the pole pieces of the core and the basis metal.

A simple magnetic tester has been described by Spencer-Timms.⁽¹⁰⁾ In principle it is based on the "steel-yard" balance and measures the force required to detach one pole of a permanent magnet from the coated steel. The thickness is derived from curves prepared with the aid of standard specimens. Cadmium, copper, zinc, chromium and brass deposits on steel can be measured, and phosphate and paint coatings are also suitable for testing with this equipment. The overall accuracy of the method is about ± 10 per cent, and it will operate

within a deposit thickness range of 0.0001 in. to 0.001 in. The basis metal can be of any thickness greater than 0.036 in.

Magnetic test devices are rapid and non-destructive, but are subject to certain limitations. The size of the testing pole is rather large and sometimes prevents testing at recesses. Curvatures of the surfaces being tested, both concave and convex, may influence the accuracy of the results seriously if at all pronounced, whilst at thicknesses of below about 0.001 in. the sensitivity of the instruments tends to be low.

POROSITY

The porosity of a coating is less significant than its thickness from the durability point of view since in general the degree of porosity decreases with increasing thickness. Porosity is, however, important in the case of deposits which are cathodic with respect to the basis metal, since in such coatings the rate of attack at the pores is likely to be accelerated. Thus it is more important that tin and nickel deposits on steel should be free from porosity than, say, zinc or cadmium coatings.

Tests for porosity are based on the application of a reagent which will react with the basis metal through pores in the coating and yet will not attack the deposit itself. For determining the porosity of cathodic coatings, such as nickel, chromium, tin, silver or copper on steel the *ferroxyl test* has been extensively used. The ferroxyl solution may be made up from:

Potassium ferricyanide	.	.	.	10 gm. per litre
Sodium chloride	.	.	.	5 gm. per litre

A piece of soft smooth rag paper is applied to the coating and dampened with the above solution by means of a brush in such a way that the paper is in close contact with the surface to be tested. It is allowed to remain for 10 minutes (further solution being applied if there is any tendency for the paper to dry) and is then removed, washed and dried. Any pores will show themselves as blue spots on the test paper.

The ferroxyl solution may have a little agar jelly usefully incorporated in it to prevent spreading of the spots.

The ferroxyl solution itself attacks nickel slightly so that thin deposits may show more porosity than is really the case. It has therefore been suggested that for thin coatings a paper dipped in a sodium chloride solution containing a little gelatine should be used in contact with the test piece. After this has been in contact with the latter for 10 minutes it is immersed in the solution of potassium ferricyanide

when blue spots will appear wherever pores are present. The latter method is also applicable to copper coatings on steel as porosity in such deposits is not readily revealed by the ferroxyl paper test. The results obtained by the ferroxyl test can only reveal a small proportion of the total pores, since pure ferricyanide solution is without action on polished iron. It is only by the addition of chloride in increasing quantity that blue spots are produced. This indicates that the surface is reactive only at discrete points, so that the reagent will only detect a pore if that pore happens to coincide with an active spot on the basis metal.

For this reason attempts have been made to find an absolute means of measuring porosity. A very promising method has recently been described by Thon and Keleman.⁽¹¹⁾ In this method the intrinsic porosity is obtained by measuring the rate of flow at extremely low pressure and under a very low overpressure of a non-corrosive gas through a plated coating which has been freed from the base metal either by peeling it off a passive base-metal surface such as stainless steel, or by dissolving the base metal in a reagent which will not attack the coating.

Experiments with this test indicate that the finer the grain structure of the deposit, the less is its intrinsic porosity. Atmospheric corrosion rapidly increases the porosity of thin deposits, probably by selective attack at local areas which open up numerous channels and increase the permeability of the coating. This may occur without any apparent massive damage to the deposit or measurable loss of weight by corrosion. In determining the porosity of a foil by this method, the apparatus is first evacuated on both sides to a pressure of about 0.001 mm. of mercury, after which one side of the apparatus is opened to atmospheric pressure. If the foil is porous the low pressure on the vacuum side will gradually rise with time at a rate dp/dt (where p is the pressure and t the time) directly proportional to the surface area of the foil F , directly proportional to the overpressure Δp , inversely proportional to the volume V on the low-pressure side, and directly proportional to a constant, k , characteristic of the given foil and expressing its particular degree of permeability; the higher the porosity the greater the value of k .

$$dp/dt = k \times F \times \Delta p / V.$$

The overpressure Δp in this procedure does not change in the course of the experiment, whether the high-pressure side is left open to the outer atmosphere or is closed after admission of the atmospheric pressure, since in the latter case the decrease of the high pressure is

negligible. Consequently Δp is constant and remains equal to the initial overpressure $\Delta p_0 = 1$ atmosphere. As all magnitudes on the right-hand side of the above equation are constant, integrating, we find that at any given time, t , the pressure p on the low-pressure side is given by the equation:

$$p = k \times F \times \Delta p_0 \times t / V$$

or

$$k = V \times p (F \times \Delta p_0 \times t).$$

If V is expressed in litres, F in sq. in., and t in minutes, the characteristic permeability constant k is expressed in litres per sq. cm. per minute.

Further work described by Thon⁽¹²⁾ indicates that under various corrosive conditions the rate of attack is very slow as measured by increasing permeability of the foil—much slower, in fact, than would be expected. Also there are very great differences between the rate of corrosive attack on electrolytic nickel deposited from different solutions, i.e. nickel from a warm chloride bath is very much more slowly attacked than from a sulphate solution. These results are not yet completely explained.

Hot Water Test.—The hot water test for porosity was originally introduced for the examination of tin-plate⁽¹³⁾ but has also found some application in the testing of nickel and other deposits. The specimens are first thoroughly cleaned, preferably by cathodic treatment in a cold 1 per cent solution of sodium carbonate; trichlorethylene degreasing alone is inadequate. They are then immersed in distilled water at a pH of 3.5 to 5.0 for a period of six hours. It may be necessary to add very dilute hydrochloric acid to reduce the water to this pH value. The water is kept at 95° C. in a tinned copper vessel, as glass vessels tend to introduce alkali into the water. At the end of the test period the samples are removed, rinsed and dried, and the number of rust-spots counted. This test is not readily applicable to electro-tinning as the rust-spots are more diffuse and are not readily counted; in this case it has been recommended that the tin surface be treated in an oxidising solution (e.g. a 10 per cent chromic acid solution at 90° C.) for five minutes to form an inhibiting film prior to the hot water test.⁽¹⁴⁾

Electrography.—Electrographic methods have been proposed as a means of showing porosity.⁽¹⁵⁾ In this procedure paper impregnated with the test electrolyte is applied to the coating and a counter electrode of a suitable metal, such as aluminium or lead placed on the other side of the paper. With ferroxyl solution the article to be tested is made the anode and with an applied e.m.f. of

5 to 6 volts any porosity is indicated in fifteen seconds. In the case of nickel on brass, porosity can be tested for by applying a filter paper moistened with a 5 per cent solution of sodium nitrate, a sheet of platinum, lead or nickel being placed on top. The test specimen is made the anode and the metal plate the cathode whilst a current of 2 milliamps per sq. in. is passed for three minutes. The filter paper is then developed for one minute in a solution of 50 gm. l. of potassium ferrocyanide and 30 gm. l. of glacial acetic acid. Porosity is shown by brown spots on the paper.

CORROSION RESISTANCE

Corrosion-resistance and porosity are closely inter-connected, but some indication of the expected life of a protective coating is obviously desirable and a great deal of attention has been given to the development of accelerated tests which will give some indication of durability. Actually, exposure tests, either accelerated or natural, should only be used for the comparison of finishes under identical conditions whilst the interpretation of the results demands the greatest care or they may lead to entirely erroneous conclusions. Exposure tests of plated coatings have been carried out on an extensive scale, the specimens being suspended usually on an inclined frame in the type of atmosphere (e.g. urban, marine, industrial, etc.) in which it is desired to carry out the test. Edges are often painted with a nitrocellulose lacquer to prevent edge effects. The methods of attaching specimens to the supporting frame and numbering them also present difficulties if they are not to interfere with the test. Recording results largely depends on personal interpretation of the appearance of the samples at the end of the test period. This period also must be carefully chosen, as clearly if the time of exposure is either too long or too short there will be little divergence in the appearance of the different specimens. The chief difficulty with exposure tests is the variability of the conditions of exposure, since no two environments or successive periods of tests are identical.

The most satisfactory means of assessing results is by the use of statistical methods which ensures that the maximum information is obtained without undue multiplicity of specimens. In itself the mere duplication of tests on a large scale is no guarantee of reliable information being obtained. The use of change in weight of specimens as a criterion of the rate of corrosion has been used, but is not always satisfactory. The use of loss of tensile strength as a measure of the rate of corrosion, particularly on wire, has also been employed, but again the method can give inconsistent results.

Salt Spray.—The use of the salt spray is very widespread as an accelerated corrosion test. Various types of apparatus have been described, but the actual design of the equipment is not of great importance provided it meets the following basic requirements:

- (1) The chamber should be constructed of non-corrodible material.
- (2) Spray jets should be arranged to produce a salt-spray fog in the chamber without direct impingement on to the specimens being tested.
- (3) The salt solution should not be re-sprayed.
- (4) Wide variations in temperature should be avoided.

Chamber Construction.—A standard form of test chamber has been recommended by the American Society for Testing Materials.⁽¹⁶⁾

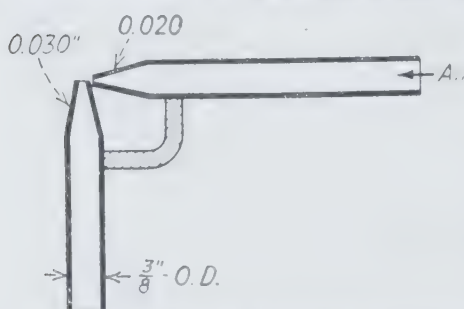


Fig. 135. — Nozzle for salt-spray apparatus

The chamber is constructed of suitable material such as slate, rubber-covered steel, stoneware, etc., and is kept at a temperature of 95° F. Arrangements are provided in the apparatus for the air supply to the nozzles (Fig. 135) to be saturated with moisture by passing it through a container filled with water at a higher

temperature than the chamber in order to counteract the drop in humidity which tends to occur by expansion at the nozzle. By maintaining the air entering the chamber at not less than 95° F. it is possible to ensure that the air is at 84 to 90 per cent relative humidity. A 20 per cent sodium chloride solution is used and the specimens are supported at about 15 degrees from the vertical. The spray is run continuously, and the amount of fog entering the chamber should be such that 0.5 to 3.0 c.c. of solution per hour are deposited for each 80 sq. cm. of horizontal area. Buffers must be provided to prevent direct impingement of the spray on to the specimens. B.S.S. 1224:1945 also describes a salt-spray test but does not specify precisely the type of apparatus to be used. The air used for producing the spray should, however, be saturated by bubbling through water prior to entering the chamber. The jets should be of glass, ebonite or Monel metal, with an internal orifice of $\frac{1}{16}$ in. The temperature of the chamber should be within the range of 18° to 25° C., and the spraying medium should be a 20 per

cent sodium chloride solution in distilled water and have a pH of 7 to 8. The author favours a rubber-lined steel chamber with Monel metal jets operated by compressed air against glass baffle-plates. The salt solution is contained in a reservoir outside the chamber, and used solution runs directly to waste.

Three per cent sodium chloride solutions and natural or synthetic sea-water have also been used as spraying media whilst others which have been recommended and employed include very dilute sulphurous acid and ammonium sulphate solutions with or without the addition of sodium chloride and other constituents, it being considered that such solutions more closely simulate corrosion in industrial atmospheres than does the salt spray.⁽¹⁷⁾ The operation of the spray may be continuous or intermittent. In the latter case the chamber is left open during a predetermined part of the cycle so that the spray dries on the surface. An alternative method is that adopted by Sutton⁽¹⁸⁾ in which the test pieces are sprayed with sea-water two or three times daily, then being allowed to dry off.

Limitations of the Test.—The salt spray is sometimes specified as a standard of durability, but this cannot be justified. There is no correlation, as extended exposure testing has shown, between salt-spray test results and service life. The salt-spray test is a useful comparative guide as between different finishing processes or to indicate quickly whether a change in operating conditions is likely to lead to reduced life. It must, however, be applied with considerable discretion, and as such it should only be employed by experts. For this reason it is of little use as an acceptance standard. It can, however, be said in broad terms that a product which will not withstand a reasonable period, say 50 hours, in the salt spray, cannot be expected to have a useful service life, but it does not follow that the converse is necessarily true.

“Tropical” Test. The author has found that rapid corrosive attack can be made to take place under “tropical” test conditions by exposing specimens to an atmosphere saturated with water vapour at 140°F. and allowing to cool twice daily so that condensation occurs.⁽¹⁹⁾ This method of test has the advantage over the salt spray in that the test more closely approximates to corrosive conditions in non-marine atmospheres.

Alternate immersion tests have also received some attention. The specimens are mounted on rods and raised and lowered into the test solution at regular periods, the time interval being usually sufficiently long to permit drying-off between successive immersions. A typical cycle would permit one minute immersion followed by 15 minutes’

exposure to the air. The corroding medium may be either the usual sodium chloride solution, or other solutions may be used. The method is less commonly used than the salt spray, but it appears in some cases to give rapid results.⁽²⁰⁾ It has also been claimed that the test is particularly selective in distinguishing between different protective methods.⁽²¹⁾

Electrochemical methods.—Potentiometric measurements have been employed as a method of determining the protective values of different coatings in various media, the changes in potential between the base and the coating metals being measured. In this way it is possible to determine whether the coating is anodic or cathodic to the basis metal, and to what extent, which may give a measure of its expected usefulness. Polarographic measurements have been similarly used. All these are rather in the nature of research methods and are apt to give misleading results unless full account of possible complicating factors is taken.

In all accelerated tests attempts to obtain a correlation between the test-life of the article and the expected life under service conditions have been abortive.

Many other forms of accelerated corrosion tests have been described from time to time but have not found any wide measure of acceptance.

ADHESION

The adhesion of an electro-deposited coating is an important measure of its serviceability, but satisfactory tests are difficult to devise. The method described by Ollard (see p. 317) provides what is probably the most accurate quantitative measure of the adhesion of a coating, but this is a specialised test requiring considerable time and equipment to enable it to be carried out. It is, moreover, not applicable where soft metal deposits such as zinc and cadmium are concerned.

One of the earliest and still the commonest method of testing adhesion is the burnishing test. It is best carried out by rubbing a smooth round steel bar to and fro across the plated surface. Poor adhesion shows itself in the development of blisters at the area of rubbing. The bar should be highly polished and may with advantage be moistened with soap solution. The test is applicable particularly to thin deposits of precious metals, nickel and chromium, and may be considered as non-destructive.

Simple bending or twisting of the plated sample is also useful as a qualitative assessment of adhesion. The specimen is bent back and forth

through an angle of 90 degrees by means of pliers until the base metal breaks; there should be no peeling or flaking of the deposit prior to this occurring. This test has been applied to electro-galvanised steel strip, and well-plated strip should withstand it without special difficulty. The rate of bending is important, as satisfactory deposits may fracture if bending is carried out too rapidly. Adhesion testing of plating on wire is generally carried out by wrapping the wire around a mandrel of its own diameter. Electro-galvanised wire will readily withstand this test.

Impact Tests.—Impact tests are useful, the simplest method being to strike the deposit repeatedly with a hammer of known weight. This type of test has recently been investigated by Hother-sall and Leadbeater⁽²²⁾ and standardised as an acceptance specification viz. the B.N.F. Adhesion Test (B.S.S. 1224). The deposit is struck repeatedly by means of a mechanical or electrically actuated hammer with a rounded head $\frac{1}{16}$ in. in diameter. The frequency of impact is at the rate of 1,500–6,000 blows per minute, the momentum of the blows being approximately $1\frac{1}{2}$ lb. in. sec. The test is applied for a period of one minute at the end of which time the coating should not have cracked or flaked. This test does not distinguish between degrees of adhesion but only serves to reject deposits of negligible adhesion which may appear satisfactory to the eye. This limitation to its applicability is admitted by the authors.

Supersonic Methods.—One of the most interesting techniques for adhesion measurement is the supersonic method which is still in the experimental stages but has considerable possibilities. Supersonic waves are generated at frequencies of from 5 to 20 megacycles per second by means of a quartz crystal apparatus usually in a liquid medium in which the test specimen is immersed. The waves are reflected back from the base metal and as the degree of adhesion changes when the detector is moved over the surface of the specimen a change in the pattern of a cathode-ray oscillogram is recorded. In its present state of development the test requires elaborate and expensive apparatus and even then it will only respond when the adhesion is practically non-existent.⁽²³⁾

Numerous other types of test have been described from time to time including high-speed centrifugal tests at 60,000 r.p.m., but none have yet provided a satisfactory means of measuring adhesion quantitatively.

Hardness and Wear-resistance.—The hardness of a coating can be determined by the usual methods such as the diamond indenter; instruments using micro-indenters are especially useful when dealing

with thin deposits. The results are, however, unreliable unless the deposit is of adequate thickness to eliminate the influence of the underlying metal. Even then, there is no means of ensuring that the hardness of a thick deposit will be the same as that of a thin one of the same metal, since it is well known that the conditions of deposition have a profound effect on hardness.

The wear and abrasion resistance are usually dependent on the hardness, and can be tested by any of the methods commonly employed in engineering research.

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APPENDIX

TABLE I

EQUIVALENT THERMOMETER SCALES

° F.	° C.	° F.	° C.	° F.	° C.	° F.	° C.
0	-17.7	51	10.5	102	38.8	250	121.1
2	-16.6	52	11.1	104	40.0	300	148.9
4	-15.5	53	11.6	106	41.1	350	176.7
6	-14.4	54	12.2	108	42.2	400	204.4
8	-13.3	55	12.7	110	43.3	450	232.2
10	-12.2	56	13.3	112	44.4	500	260.0
12	-11.1	57	13.8	114	45.5	550	287.8
14	-10.0	58	14.4	116	46.6	600	315.6
16	-8.8	59	15.0	118	47.7	650	343.3
18	-7.7	60	15.5	120	48.8	700	371.1
20	-6.6	61	16.1	122	50.0	750	398.9
22	-5.5	62	16.6	124	51.1	800	426.7
24	-4.4	63	17.2	126	52.2	850	454.4
26	-3.3	64	17.7	128	53.3	900	482.2
28	-2.2	65	18.3	130	54.4	950	510.0
30	-1.1	66	18.8	132	55.5	1000	537.8
32	0.0	67	19.4	134	56.6	1050	565.5
33	0.5	68	20.0	136	57.7	1100	593.3
34	1.1	69	20.5	138	58.8	1150	621.1
35	1.6	70	21.1	140	60.0	1200	648.9
36	2.2	72	22.2	142	61.1	1250	676.7
37	2.7	74	23.3	144	62.2	1300	704.4
38	3.3	76	24.4	146	63.3	1350	732.2
39	3.8	78	25.5	148	64.4	1400	760.0
40	4.4	80	26.6	150	65.5	1450	787.8
41	5.0	82	27.7	152	66.6	1500	815.5
42	5.5	84	28.8	154	67.7	1550	843.3
43	6.1	86	30.0	156	68.8	1600	871.1
44	6.6	88	31.1	158	70.0	1650	898.9
45	7.2	90	32.2	160	71.1	1700	926.7
46	7.7	92	33.3	170	76.6	1750	954.4
47	8.3	94	34.4	180	82.2	1800	982.2
48	8.8	96	35.5	190	87.7	1850	1010.0
49	9.4	98	36.6	200	93.3	1900	1037.8
50	10.0	100	37.7	212	100.0	2000	1093.3

TABLE II
DENSITY CONVERSION TABLES

Sp. Gr.	° Bé.	° Tw.	lb. per cu. ft.
1.005	0.72	1	62.682
1.025	3.54	5	63.929
1.050	6.91	10	65.488
1.075	10.12	15	67.048
1.100	13.18	20	68.607
1.125	16.11	25	70.166
1.150	18.91	30	71.725
1.175	21.60	35	73.285
1.200	24.17	40	74.844
1.225	26.63	45	76.403
1.250	29.00	50	77.962

TABLE III

CONVERSION FACTORS

	<i>Multiplication factor</i>
Inches to centimetres	2.54
Centimetres to inches	0.394
Gallons to litres	4.5
Litres to gallons	0.22
Pounds to kilogrammes	0.45
Kilogrammes to pounds	2.2
Cubic feet to cubic metres	0.028
Cubic metres to cubic feet	35.3
Ounces per gallon to grammes per litre	6.25
Grammes per litre to ounces per gallon	0.161
Grammes per litre to Troy ounces per gallon	0.146
Troy ounces per gallon to grammes per litre	9.8
Pennyweights per gallon to grammes per litre	0.49
Grammes per litre to pennyweights per gallon	2.73
Ampères per square foot to ampères per square decimetre	0.108
Ampères per square decimetre to ampères per square foot	9.29
Grammes per square decimetre to ounces per square foot	0.328
Ounces per square foot to grammes per square decimetre	3.24

Note: The Imperial gallon is equal to 1.20 U.S. gallons.

TABLE IV

METAL CONTENTS OF SOME METALLIC SALTS

Salt	Formula	Metal Content per cent
Cadmium cyanide	$\text{Cd}(\text{CN})_2$	68.3
Cadmium oxide	CdO	87.6
Chromic acid	CrO_3	52.0
Chevreul's salt	$\text{Cu}_2\text{SO}_3, \text{CuSO}_3, 2\text{H}_2\text{O}$	49.3
Cobalt sulphate	$\text{CoSO}_4, 7\text{H}_2\text{O}$	21.0
Copper carbonate (basic)	$\text{CuCO}_3, \text{Cu}(\text{OH})_2$	57.5
Copper cyanide	CuCN	71.0
Copper sulphate	$\text{CuSO}_4, 5\text{H}_2\text{O}$	25.5
Gold chloride	AuCl_3	64.9
Lead carbonate (basic)	$2\text{PbCO}_3, \text{Pb}(\text{OH})_2$	80.1
Nickel sulphate	$\text{NiSO}_4, 7\text{H}_2\text{O}$	20.91
Nickel ammonium sulphate	$\text{NiSO}_4, (\text{NH}_4)_2\text{SO}_4, 6\text{H}_2\text{O}$	14.9
Nickel chloride	$\text{NiCl}_2, 6\text{H}_2\text{O}$	24.7
Silver cyanide	AgCN	80.6
Sodium Stannate	$\text{Na}_2\text{SnO}_3, 3\text{H}_2\text{O}$	44.5
Stannous sulphate	SnSO_4	55.1
Stannous chloride	$\text{SnCl}_2, 2\text{H}_2\text{O}$	52.7
Zinc cyanide	$\text{Zn}(\text{CN})_2$	55.7
Zinc sulphate	$\text{ZnSO}_4, 7\text{H}_2\text{O}$	22.8

TABLE V

APPROXIMATE CATHODE EFFICIENCIES OF SOME PLATING SOLUTIONS

<i>Solution</i>	<i>Efficiency (per cent)</i>
Cadmium	90-95
Chromium	10-15
Copper (sulphate)	96-100
Copper (cyanide)	40-65
Gold	70-90
Lead (fluoborate)	95-100
Nickel	95-98
Silver	98-100
Tin (acid)	85-95
Tin (Stannate)	70-85
Rhodium	10-20
Zinc (sulphate)	90-95
Zinc (cyanide)	85-90

TABLE VI

RATE OF DEPOSITION OF NICKEL
(CATHODE EFFICIENCY 95 %)

Thickness of Deposit (in.)	Weight (oz. sq. ft.)	Time (mins.) required for deposition at various current densities (amps. per sq. ft.)			
		10 amp.	15 amp.	25 amp.	40 amp.
0.0001	0.074	11.81	7.9	4.7	3.0
0.0002	0.148	23.6	15.7	9.5	5.9
0.0003	0.222	35.4	23.6	14.2	8.9
0.0004	0.296	47.2	31.5	18.9	11.8
0.0005	0.370	59.1	39.4	23.7	14.8
0.0006	0.444	70.9	47.2	28.4	17.7
0.0007	0.518	82.7	55.1	33.1	20.7
0.0008	0.592	94.5	63.0	37.8	23.6
0.0009	0.666	106.3	70.8	42.6	26.6
0.0010	0.740	118.1	78.7	47.3	29.5

TABLE VII

RATE OF DEPOSITION OF COPPER FROM COPPER CYANIDE SOLUTION
(CATHODE EFFICIENCY 95 %)

Thickness of Deposit (in.)	Weight (oz. sq. ft.)	Time (mins.) required for deposition at various current densities (amps. per sq. ft.)			
		10 amp.	15 amp.	25 amp.	40 amp.
0.0001	0.074	5.6	3.7	2.2	1.4
0.0002	0.148	11.1	7.4	4.4	2.8
0.0003	0.222	16.7	11.1	6.7	4.2
0.0004	0.296	22.2	14.8	8.9	5.6
0.0005	0.370	27.8	18.6	11.1	7.0
0.0006	0.444	33.4	22.3	13.3	8.3
0.0007	0.518	38.9	26.0	15.5	9.7
0.0008	0.592	44.5	29.7	17.8	11.1
0.0009	0.666	50.0	33.4	20.0	12.5
0.0010	0.740	55.6	37.1	22.2	13.9

TABLE VIII

RATE OF DEPOSITION OF COPPER FROM ACID COPPER SOLUTION
(CATHODE EFFICIENCY 100%)

Thickness of Deposit (in.)	Weight (oz. sq. ft.)	Time (mins.) required for deposition at various current densities (amps. per sq. ft.)			
		10 amp.	15 amp.	25 amp.	40 amp.
0.0001	0.074	10.6	7.1	4.3	2.7
0.0002	0.148	21.2	14.2	8.5	5.3
0.0003	0.222	31.9	21.2	12.8	8.0
0.0004	0.296	42.5	28.3	17.0	10.6
0.0005	0.370	53.1	35.4	21.3	13.3
0.0006	0.444	63.7	42.5	25.5	16.0
0.0007	0.518	74.3	49.6	29.8	18.62
0.0008	0.592	85.0	56.6	34.0	21.3
0.0009	0.666	95.6	63.7	38.3	23.9
0.0010	0.740	106.2	70.8	42.5	26.6

TABLE IX

RATE OF DEPOSITION OF CADMIUM
(CATHODE EFFICIENCY 95%)

Thickness of Deposit (in.)	Weight (oz./sq. ft.)	Time (mins.) required for deposition at various current densities (amps. per sq. ft.)			
		10 amp.	15 amp.	25 amp.	40 amp.
0.0001	0.071	6.1	4.1	2.5	1.5
0.0002	0.142	12.3	8.2	4.9	3.1
0.0003	0.213	18.4	12.3	7.4	4.6
0.0004	0.284	24.5	16.4	9.8	6.1
0.0005	0.355	30.7	20.5	12.3	7.7
0.0006	0.426	36.8	24.5	14.7	9.2
0.0007	0.497	42.9	28.6	17.2	10.7
0.0008	0.568	49.0	32.7	19.6	12.2
0.0009	0.639	55.2	36.8	22.1	13.8
0.0010	0.710	61.3	40.9	24.5	15.3

TABLE X

RATE OF DEPOSITION OF ZINC FROM ACID AND CYANIDE ZINC SOLUTIONS
(CATHODE EFFICIENCY 95 %)

Thickness of Deposit (in.)	Weight (oz. sq. ft.)	Time (mins.) required for deposition at various current densities (amps. per sq. ft.)			
		10 amp.	15 amp.	25 amp.	40 amp.
0.0001	0.059	8.7	5.8	3.5	2.2
0.0002	0.118	17.3	11.5	6.9	4.3
0.0003	0.177	26.0	17.3	10.4	6.5
0.0004	0.236	34.6	23.1	13.8	8.6
0.0005	0.295	43.3	28.9	17.3	10.8
0.0006	0.354	51.9	34.6	20.8	13.0
0.0007	0.413	60.6	40.4	24.2	15.1
0.0008	0.472	69.2	46.2	27.7	17.3
0.0009	0.531	77.9	51.9	31.1	19.4
0.0010	0.590	86.5	57.7	34.6	21.6

TABLE XI

RATE OF DEPOSITION OF CHROMIUM
(CATHODE EFFICIENCY 15 %)

Thickness of Deposit (in.)	Weight (oz. sq. ft.)	Time (mins.) required for deposition at various current densities (amps. per sq. ft.)			
		80 amp.	90 amp.	100 amp.	150 amp.
0.00001	0.0059	2.6	2.3	2.1	1.4
0.00002	0.0118	5.2	4.6	4.1	2.8
0.00003	0.0177	7.8	6.9	6.2	4.1
0.00004	0.0236	10.4	9.2	8.3	5.5
0.00005	0.0295	13.0	11.5	10.4	6.9
0.00006	0.0354	15.5	13.8	12.4	8.3
0.00007	0.0413	18.1	16.1	14.5	9.7
0.00008	0.0472	20.7	18.4	16.6	11.0
0.00009	0.0531	23.3	20.7	18.6	12.4
0.00010	0.0590	25.9	23.0	20.7	13.8

TABLE XII

RATE OF DEPOSITION OF SILVER
(CATHODE EFFICIENCY 100%)

Thickness of Deposit (in.)	Weight (Troy oz./sq. ft.)	Time (mins.) required for deposition at various current densities (amps. per sq. ft.)			
		2 amp.	3 amp.	4 amp.	5 amp.
0.0001	0.079	18.6	12.4	9.3	7.4
0.0002	0.158	37.2	24.8	18.6	14.9
0.0003	0.237	55.8	37.2	27.9	22.3
0.0004	0.316	74.4	49.6	37.2	29.8
0.0005	0.395	93.0	62.0	46.5	37.2
0.0006	0.474	111.6	74.4	55.8	44.6
0.0007	0.553	130.2	86.8	65.1	52.1
0.0008	0.632	148.8	99.2	74.4	59.5
0.0009	0.711	167.4	111.6	83.7	67.0
0.0010	0.790	186.0	124.0	93.0	74.4

TABLE XIII

CONVERSION TABLE

	Oz.		Gm.	Dwt. Troy	Equivalent thickness in. per sq. ft.
	Avoir.	Troy			
1 oz. (avoir.)	1.0	0.911	28.35	18.23	0.000633
1 oz. (troy)	1.097	1.0	31.10	20.0	0.000683
1 dwt. (troy)	0.0549	0.05	1.555	1.0	0.0000341
1 gm.	0.0353	0.0322	1.0	0.643	0.0000219

TABLE XIV
CHEMICAL AND ELECTRO-CHEMICAL CONSTANTS OF METALS

	Symbol	Atomic weight	Specific gravity	Valency	Chemical equivalent	Gm. per amp. hr. deposited at 100 per cent. efficiency	Thickness deposited per hour at 10 amps./sq. ft. at 100 per cent. efficiency (in.)
Cadmium	Cd	112.4	8.65	2	56.2	2.0968	0.00104
Chromium*	Cr	52.0	7.1	6	8.7	0.3234	0.00020
Cobalt	Co	58.9	8.9	2	29.5	1.0094	0.00055
Copper (cyanide)	Cu	63.6	8.93	1	63.6	2.3716	0.00113
Copper (sulphate)	Cu	63.6	8.93	2	31.8	1.1858	0.00056
Gold (chloride)	Au	197.2	19.3	3	65.7	2.4523	0.00054
Gold (cyanide)	Au	197.2	19.3	1	197.2	7.3569	0.00161
Iron (sulphate)	Fe	55.8	7.9	2	27.9	1.0420	0.00055
Iron (chloride)	Fe	55.8	7.9	3	18.6	0.6946	0.00082
Lead	Pb	207.2	11.35	2	103.6	3.8654	0.00148
Nickel	Ni	58.7	8.9	2	29.3	1.0948	0.00053
Rhodium	Rh	102.9	12.4	3	34.3	1.2797	0.00042
Silver	Ag	107.9	10.5	1	107.9	4.0274	0.00162
Tin (chloride)	Sn	118.7	7.3	2	59.4	2.2142	0.00140
Tin (sulphate)	Sn	118.7	7.3	2	59.4	2.2142	0.00140
Tin (stannate)	Sn	118.7	7.3	4	29.7	1.1071	0.00070
Zinc (cyanide)	Zn	65.4	7.14	2	32.7	1.1816	0.00073
Zinc (sulphate)	Zn	65.4	7.14	2	32.7	1.1816	0.00073

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